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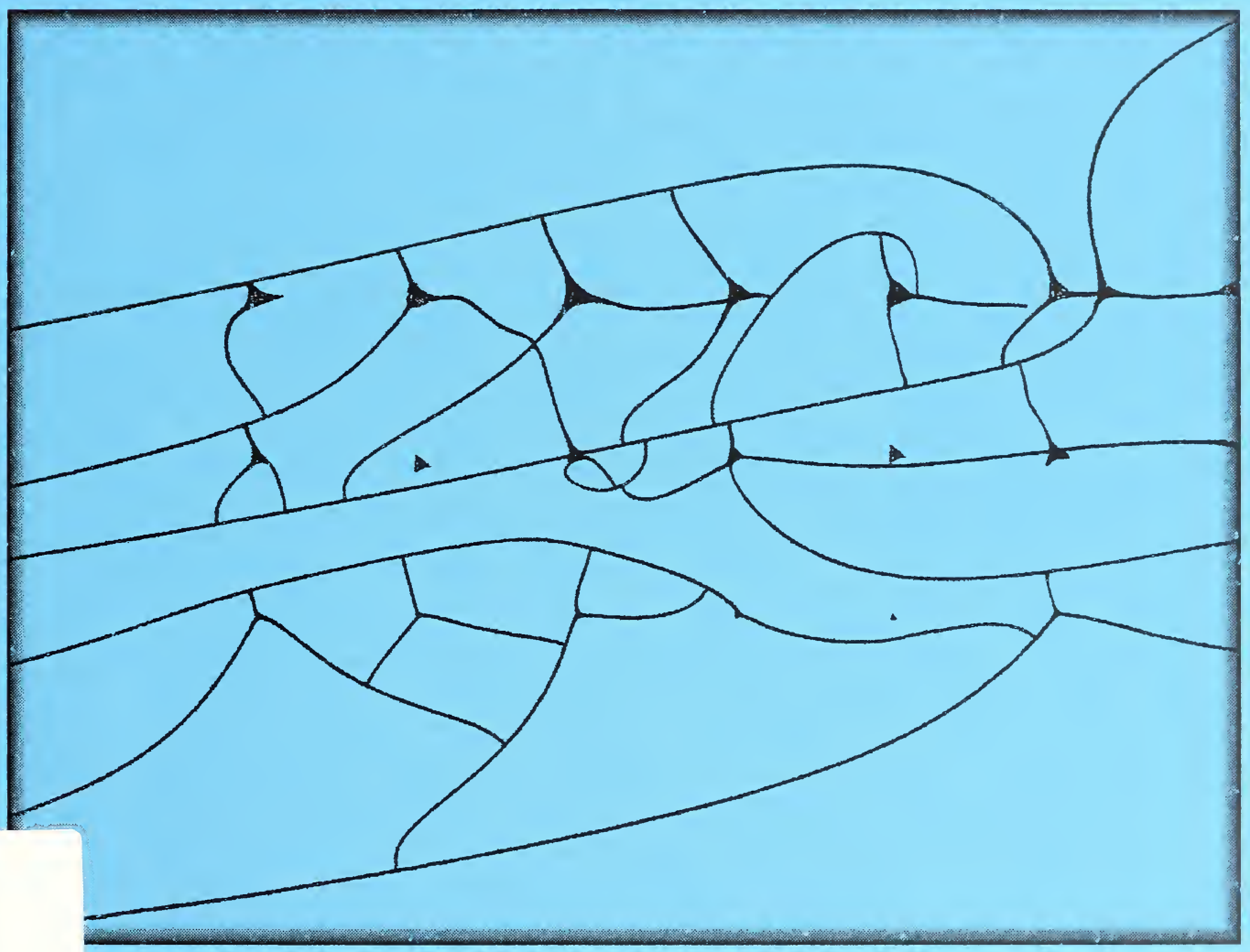

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NISTIR 6063
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities 1997

Instrumented Indentation Photograph

The image on the front cover depicts tensile cracking induced by Berkovich indentations in a 1.0 μm thick amorphous silicon nitride film on a crown glass surface. Indentation spacing was 75 μm x 75 μm. Indentation loads applied were 700 mN, 300 mN and 90 mN (top, middle and bottom rows, respectively.) This research was generated during a collaboration between NIST and the Federal Institute for Materials Research and Testing (BAM). The expected outcome from this collaboration is the development of standard reference coatings for instrumented indentation and for scratch and wear testing.

MSEL

Materials Science and Engineering Laboratory

CERAMICS

S.W. Freiman, Chief
S.J. Dapkunas, Deputy

NISTIR 6063
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and Technology

Technical Activities 1997

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TECHNOLOGY ADMINISTRATION
Gary Bachula, Acting Under Secretary for Technology
NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY
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Organization Chart
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Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for that purpose.

EXECUTIVE SUMMARY

As reflected in this Report, the activities of the NIST Ceramics Division in 1997 continued to be organized in the form of Programs, emphasizing a desire to foster collaborations within the Ceramics Division as well as throughout the Materials Science and Engineering Laboratory, and to conduct focused activities on a scale that can lead to greater benefits for the U.S. ceramics community. The Programs are made up of projects whose primary goal is the development of measurement techniques and standards. Activities such as the development of Standard Reference Materials are integrated within the relevant Programs. At the same time, we continue to maintain a Division management structure in the form of Groups.

The participation of U.S. industry in all phases of the research has been strongly encouraged. Three consortia typify our desire to involve U.S. companies as well as universities and other government laboratories in the research leading to improved measurement procedures.

The first, the Ceramic Machining Consortium, is being led by Dr. Said Jahanmir and currently consists of twenty members including ceramic producers and finishers, manufacturers of ceramic machining equipment, automotive companies, and universities. The work within this Consortium has led to a fundamental understanding of the damage that can be caused in ceramic parts due to various factors in the machining process. Based on this understanding it has been demonstrated that in many instances material removal rates of advanced ceramics such as silicon nitride can be increased significantly above those obtained current practice without causing degradation in properties, thereby leading to reduced machining costs.

A Consortium of four biomaterials companies under the joint leadership of Dr. Stephen Hsu and Dr. John Tesk of the Polymers Division is developing wear test procedures for materials being used in total joint replacements. These procedures will enable companies to more rapidly bring improved biomaterials to market.

A new Consortium was begun in 1997 under the leadership of Dr. George Onoda. The Ceramic Processing Characterization Consortium (CPCC) was formed with a goal of establishing a strong measurements and characterization infrastructure for the U.S. ceramic processing industry. As of November, 1997, Memoranda of Understanding have been signed: involving 50 companies, 10 universities, and 4 government laboratories and agencies. At the initial meeting of the CPCC in June, 1997, five project teams were formed focusing on issues important for ceramic processing.

We have continued to monitor the direction of U.S. industrial interests in ceramic materials. Based on these observations, we have expanded our activities on ceramics for microwave communication to include joint research with the Electromagnetic Fields Division at NIST, Boulder, on dielectric measurements of new compounds identified in the phase equilibria studies being carried out under the direction of Dr. Terrell Vanderah. Also, in 1997 we formed a new program entitled Thin Film Measurement and Standards. This Program, being led by Dr. Grady White, is developing a wide range of measurement procedures critical for the rapidly growing area of functional ceramic films.

The Ceramics Division had the following significant accomplishments and impacts during FY 1997.

- A new consortium called the Ceramic Processing Characterization Consortium (CPCC) was formed. The purpose of the CPCC is to develop a stronger measurements infrastructure for the U. S. ceramic processing industry. The current membership consists of 85 individuals from 50 companies, 4 National Laboratories and NIST, and 10 universities.

- The primary crystallization field of the five-component Pb-BSCCO 2223 high-temperature superconductor (Tc = 110 K) has been determined. This result is important for industry in order to design processing temperature-composition paths that will yield optimum superconducting wires and tapes.

- Two major sources of severe yield variability in lithium niobate, proton- exchanged, guided wave, modulators were identified using synchrotron high resolution diffraction imaging. This understanding has led to significantly enhanced device yields.

- Software was written that, for the first time, allows conventional powder x-ray diffractometers to be used to quantify the degree of texture in a ceramic microstructure. This software has been made available on the World Wide Web.

- Small-angle neutron and x-ray scattering measurements carried out on infrastructural cements and concretes have established a link between the coarse features in the particle morphology of silica fumes and the microstructural development of the hydrating cement blends. This information is expected to lead to improved cementitious materials.

- The measurement of the adhesion of monomolecular films, critical to the durability of components in magnetic hard discs, sensors, et al., is complicated by tribochemical reactions from surface contacts. A newly developed technique, involving scratching using submicrometer diamond particles to simulate contacts, opens the way to measure the effect of tribochemistry on adhesion under in-service conditions.

- As part of an NIH supported study of machining of dental ceramics, measurements of surface damage have led to the conclusion that dental burs with coarse diamond particles can produce large cracks which can reduce the strength and wear resistance of teeth and ceramic restorations.

- The beta version of an Object-Oriented Finite element program (OOF), developed in collaboration with ITL and CTCMS, was made available on the World Wide Web. More than 100 copies of this program, which represents a new paradigm for understanding physical properties of real, complex, microstructures, have already been downloaded.

- The Ceramics Division has ported the PC version of the NIST Standard Reference Database on High Temperature Superconducting Materials to the World Wide Web. This database provides evaluated thermal, mechanical, and superconducting property data for oxide superconductors.

- Four new Standard Reference Materials were certified: SRM 1996, giving the distribution in size of a zirconia powder used in thermal spray; SRM 1018b and SRM 1019b, glass spheres with different size ranges used to determine ceramic powder sizes, and S.M. 1899, certifying the specific surface area of a silicon nitride powder.

- Pratt & Whitney modified their spray dried zirconia feedstock binder content specification to improve coating performance as a result of a collaborative project.

- As a result of this collaborative effort, one of the consortium members has invested in a new state-of-the-art machine tool for high rate grinding. Other consortium members have transferred the NIST data to their engineers and have shared the data with their customers for implementation in process design.

Stephen W. Freiman
Chief, Ceramics Division

TECHNICAL ACTIVITIES

CERAMIC COATINGS

CERAMIC COATINGS

The Ceramic Coatings Program is a measurement and characterization effort which addresses the processing reproducibility and performance prediction issues that are primarily associated with thermal-spray deposited ceramic coatings. The program focuses on plasma-spray-deposited ceramic thermal barrier coatings used in aircraft gas turbines and expected to be used in land-based turbines and diesel engines. Sales in the thermal-spray industry are currently valued at more than one billion dollars annually, a significant portion of which is ceramic thermal-barrier coatings. Collaborations have been established with industrial organizations including Pratt and Whitney, General Electric, Caterpillar, METO, Madoc and Zircon as well as the Thermal Spray Laboratory at the State University of New York at Stoney Brook and the Thermal Spray Laboratory at Sandia National Laboratory. The program includes collaboration with the National Aerospace Laboratory and the National Mechanical Engineering Laboratory, both in Japan, to examine functionally gradient materials. Collaboration is also underway with BAM (Germany) for the development of characterization techniques for thin, hard films. Research is conducted on the processing and properties of Physical Vapor Deposited (PVD) ceramic coatings in collaboration with Praxair, an Advanced Technology Program (ATP) awardee.

Participants in the NIST program are located in the Ceramics, Materials Reliability, and NIST Center for Neutron Research of the Materials Science and Engineering Laboratory as well as the Chemical Science and Technology Laboratory.

The approach taken in the plasma-spray (PS) research has been to build on the analytical capabilities at NIST and the material processing capabilities of collaborators. The program has the following elements:

- development of techniques for characterization of physical and chemical properties of stabilized zirconia and tungsten carbide feedstock to provide data for increased processing reproducibility as well as data required for production of a Standard Reference Material suitable for calibration of light-scattering size distribution instruments used in industry for analysis of PS powder;

- development of scattering techniques to determine the quantity, size and orientation of porosity and microcracks in PS ceramic coatings suitable for use in modeling the thermomechanical behavior of these materials;

- development of methods to measure chemical, elastic modulus, and thermal properties on a scale suitable for use in microstructural models of behavior;

- development of techniques to model thermomechanical behavior of thermal-barrier coatings to enable more reliable performance prediction; and

- development of techniques for accurate measurement of the thermal conductivity of PS

coatings, by use of the guarded hot-plate technique suitable for incorporation in ASTM standards and by the pulsed laser heating technique, to provide a method for comparison with routine industrial techniques.

- development and refinement of more sensitive methods for accurate analysis of oxide phases and residual stresses which affect performance and durability of coatings.

Research on chemical mapping of powders and microstructures is conducted in the Microanalysis Division of the Chemical Science and Technology Laboratory. Thermal property research is conducted in the Materials Reliability and Metallurgy divisions and the Center for Neutron Research participates in both the powder analysis and scattering projects. A strong attribute of the PS coatings research is the use of common materials for which complementary data can provide a more complete understanding of processing-microstructure-property relationships.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Characterization of Thermal Spray Zirconia Powders

Principal Investigators: Stanley J. Dapkunas, Patrick Pei, James F. Kelly, Judith Stalik (Center for Neutron Research) and Eric Steel (Chemical Science and Technology Laboratory)

Technical Objective:

The objective of this research is to develop measurement methods for those characteristics of thermal spray feedstock which determine the microstructure and properties of ceramic coatings.

Technical Description:

This research is conducted in cooperation with the thermal spray industry, universities and government laboratories. Feedstock powders are an important determinant of the final microstructure, and hence properties, and wear resistance of coatings. Important powder characteristics include particle size distribution, chemistry, phase content, flow, and thermal properties.

Collaborative research has emphasized NIST powder characterization and plasma spray deposition by others with joint analysis to relate powder properties to process parameters, microstructure, and performance. Earlier research addressed the role of organic binders in zirconia feedstock on the thermal shock behavior of coatings and the role of particle size distribution on spray behavior. Subsequent research has been conducted in cooperation with a broad range of powder producers, plasma spray equipment and analytical instrument manufacturers, and coatings producers and culminated in the development of S.M. 1982 for the calibration of particle size distribution measurement instruments. This research has been extended to the development of an S.M. for size distribution of tungsten carbide/cobalt feedstock, important for wear resistant coatings.

The program attempts to develop a comprehensive understanding of the interrelationships between powder, deposition behavior and microstructure/properties. This is accomplished by conducting a broad range of characterizations on a given powder or deposit. In this vein, additional research in collaboration with the Sandia National Laboratory has utilized the same powder (S.M. 1982) to determine the role of size fractions on behavior in the plasma spray process.

External Collaborations:

Technical collaboration with organizations representing engine manufacturers, material manufacturers, spray equipment and instrument suppliers includes: Pratt & Whitney, General Electric, Caterpillar, Praxair, METO, Zircon, TAFA, Metech, H. C. Stark, Leeds and Northrup,

Horiba, Sandia National Laboratory, OSRam/Sylvania, and the State University of New York at Stony Brook.

Planned Outcome:

The planned outcome of this research is the development of analytical methods which will enable manufacturers to improve process and material specifications.

Accomplishments:

- An empirical relationship between the binder content of spray dried zirconia and thermal shock behavior of coatings was established.

- S.M. 1982, Plasma Spray Zirconia-Particle Size Distribution was issued in November, 1996.

- Collaborative research with Sandia National Laboratory was conducted under the auspices of a NIST/SNL memorandum of understanding (MOU) and the behavior of S.M. 1982 feedstock in a plasma plume was determined as a function of size cut.

- A small angle neutron scattering technique was developed for the unambiguous analysis of the zirconia monoclinic phase.

Publications:

Characterization and Processing of Spray-Dried Zirconia Powders for Plasma Spray Application, P. Pei, S. G. Malghan, S. J. Dapkunas, and P. H. Zajchowski, Journal of Thermal Spray Technology, Volume 5 (3) September 1996, 343-351.

Analysis of Zirconia Powder for Thermal Spraying: Reference Material for Particle Size Distribution Measurement, P. Pei, J. Kelly, S. Malghan and S. Dapkunas, Proceedings of the National Thermal Spray Conference, October, 1996, "Thermal Spray: Practical Solutions for Engineering Problems", C. C. Berndt (Ed), ASM International, Ohio, USA, 263-273.

Measurement Methods and Standards for Processing and Application of Thermal Barrier Coatings, S. J. Dapkunas, Journal of Thermal Spray Technology, Volume 6(1) March 1997, 67-76.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Mechanical Property Evaluation and Test Development

Principle Investigators: Douglas Smith and Jay Wallace

Technical Objectives:

- To organize workshops and symposia that will bring the instrumented indentation community towards consensus on recommended test and analysis procedures, and to participate in indentation round robins; and, in conjunction with other standards laboratories (BAM, NPL), to prepare and characterize possible candidates for coating-substrate standard reference materials (S.M.'s) for mechanical testing.

- To collect experimental indentation data (load-displacement curves) and correlate them with analytical and numerical modeling of the indentation process, in order to better understand deformation mechanisms beneath indenters, particularly in film-substrate and multilayer systems.

- To use instrumented indentation to quantify hardness, Young's modulus, porosity and microcrack density in ceramic coatings, both to characterize as-prepared coatings and to quantify damage evolution; and to study the microstructural damage done during the indentation of brittle coatings and bulk material and, when possible, to correlate that damage with other material properties such as machinability and wear resistance that depend on microfracture processes.

- To investigate the effect of changing fabrication conditions and post fabrication annealing on the elastic modulus of free standing air plasma sprayed ZrO_2 deposits and correlate these changes with changes in microstructure found by small angle neutron scattering and scanning electron microscopy.

Technical Description:

The project uses two instrumented indenters (one a commercial nanoindenter and one a NIST-modified microhardness machine) to probe the mechanical properties of bulk materials and thin films. Taken together, the two machines permit indentation studies at peak indentation loads ranging from 40 μN to 40 N, using Vickers, Berkovich and spherical diamond and WC-Co indenter tips. The resulting experimental load-displacement curves are analyzed to yield the hardness and Young's modulus of the material probed, as well as the energy absorbed in the indentation process. Since elastic modulus is sensitive to discontinuities in the microstructure, such as cracks and crack-like voids, measurements such as these are well suited for examining the changes that occur as the result of changing fabrication conditions or post-fabrication treatments. Relatively small areas of material are probed, permitting local mapping of elastic modulus variations.

The focus of the program is on the development of the *technique* of instrumented indentation, rather than the application of the technique to particular material systems, although data are taken on specific materials of technological interest (*e.g.*, thermal barrier and wear-resistant coatings, dental restoration materials, and S.M. candidates). International workshops, symposia, and round robin standards tests are organized and executed in an effort to guide the instrumented indentation community toward greater standardization in data analysis, to the expand the range of mechanical property characterization possible with the technique, and to develop physical standards for the technique.

External Collaborations:

- National Physical Laboratory (NPL), U.K., and Tokyo University, Japan: Design and execution of VAMAS instrumented indentation round robin testing of model film-substrate systems.

- Federal Institute for Materials Research and Testing (BAM), Berlin: Development of reference coatings using indentation and spectroscopic ellipsometry.

- Praxair Surface Technologies: Characterization of TiN and CrN coatings developed as replacements for chrome plating in wear applications.

- Institute of Plasma Physics, Academy of Sciences of the Czech Republic: Study of processing and property evolution of free standing air plasma sprayed ZrO_2 deposits.

- Department of Material Science and Bioengineering, AIST, MITI, Japan: Study of functionally graded materials prepared by plasma arc sintering.

- Kansas State University: Mechanical properties studies of Group III nitride thin films (AlN, BAlN, InN) for electronic and optoelectronic applications.

Planned Outcomes:

Recommended guidelines for instrumented indentation testing and analysis procedures will help researchers with different indentation systems at different laboratories compare results effectively. Bulk and film standard reference materials will aid in machine calibrations.

Reliable mechanical property data at small length scales will aid designers of thin-film and multilayer structures.

Changes in the crack/void structure of plasma sprayed thermal barrier coatings, due either to changing processing conditions or in service annealing, can have a significant influence in the resulting properties, and thus must be well characterized and understood. Instrumented indentation measurements such as these provide a sound basis for characterizing these changes.

The use of instrumented indentation to introduce and quantify microcrack damage may lead to the use of the technique to predict wear resistance and fracture toughness.

Accomplishments:

In collaboration with the National Physical Laboratory in England and Tokyo University, a new VAMAS Technical Working Area has been started (TWA 22: Mechanical Properties of Thin Coatings), and the first project has begun (Hardness and Modulus Measurement Using Depth Sensing Indentation). Sets of film/substrate specimens have been distributed, and preliminary results are being analyzed.

The first year of a three year collaboration with BAM on the development of reference coatings has been completed. Dr. Uwe Beck of BAM was a guest scientist at NIST for five months, working with Douglas Smith to characterize several candidates for a possible joint NIST/BAM reference coating system for mechanical and optical applications. Coatings of SiO_2 and Si_3N_4 in 0.1 μm and 1.0 μm thicknesses, as well as an SiO_2/Si_3N_4 multilayer, were studied in detail using nanoindentation, x-ray diffraction and spectroscopic ellipsometry, and were found to be promising as potential reference systems. The work will continue in 1998 with a guest scientist from NIST working at BAM.

Extensive measurements have been made of the mechanical properties of several zirconia air-plasma-sprayed thermal barrier coatings. It was found that the elastic moduli varied not only through the thickness of the deposit, due to self annealing from subsequent passes of the plasma torch, but also varied depending on whether the measurement direction was parallel to the plasma spray direction or perpendicular to it. Significant increases in elastic modulus were found in samples annealed for 2.5 h at 1100 °C. These changes have been correlated with small angle neutron scattering measurements of void surface area as well as with qualitative observation of cracking in the microstructure.

One symposium on mechanical property testing for coatings was held as part of the International Conference on Metallurgical Coatings and Thin Films, April, 1997, in San Diego. Another is currently being organized for April, 1998. An ASTM workshop on the technique is being organized for the November, 1998, ASTM meeting in Norfolk, VA.

Publications:

J.H. Edgar, D.T. Smith, C.R. Eddy, C.A. Carosella and B.D. Sartwell, "C-Boron-Aluminum Nitride Alloys Prepared by Ion-Beam-Assisted Deposition." Thin Solid Films **298** 33-38 (1997).

J.H. Edgar, C.H. Wei, D.T. Smith, T.J. Kistenmacher and W.A. Bryden, Hardness, Elastic Modulus and Structure of Indium Nitride Thin Films on AlN-Nucleated (00.1) Sapphire Substrates. J. Mater. Science: Electronic Materials **8** 307-312 (1997).

H.H.K. Xu, D.T. Smith, S. Jahanmir, E. Romberg, J.R. Kelly, V.P. Thompson and E.D. Rekow, Indentation Damage and Mechanical Properties of Human Enamel and Dentin. Accepted by J. Dental Research.

J. S. Wallace and J. Ilavsky, Elastic Modulus Measurements in Plasma Sprayed Deposits, Proceedings of 10th National Thermal Spray Conference.

J. S. Wallace and J. Ilavsky, Elastic Modulus Measurements in Plasma Sprayed Deposits,. Submitted to Journal of Thermal Spray Technology.

PROGRAM NAME: Ceramic Coatings

PROJECT TITLE: Modeling of Coating Microstructure and Failure

Principal Investigators: Edwin R. Fuller, Jr., W. Craig Carter, and Jay S. Wallace

Technical Objectives:

The objective of this research is to develop computational models of micromechanical behavior, fracture, deformation, damage, and other nonlinear phenomena, in real and simulated microstructures of ceramic coatings. A technique for obtaining the average linear response from selected microstructural regions is envisioned, thereby providing data on local and bulk properties. Predictions of response for simulated and digital representations of actual microstructures with subsequent comparison to measured properties are a primary goal. Efficient storage and microstructural representation techniques are to be developed.

Technical Description:

This research models the mechanics and physics of heterogeneous microstructures of ceramic coatings at the mesoscopic level and develops computationally efficient algorithms and computational codes for simulating the micromechanical behavior of these materials. New methods are developed to simulate concurrent physical phenomena in realistic coating microstructures. Surface and subsurface damage of thermal barrier coating systems produced by contact loading is quantified using finite element method. Additionally, the project seeks to develop computationally efficient algorithms for simulations of the microstructural development in these materials.

External Collaborations:

Chuanshu Ji and Robert Derr, Dept. of Statistics, University of North Carolina, Chapel Hill, NC, are collaborating in the development of statistical tools for generating and quantifying microstructural features.

Planned Outcome:

This study is expected to establish a more accurate model of the effect of porosity on elastic properties.

Accomplishments:

An object-oriented finite element code (OOF) was developed, and used to study both simulated and actual coating microstructures. Averaged elastic properties of thermal barrier coatings were calculated on a microstructural basis from digitized images and compared with experimental measurements. The computational simulations were performed on random regions from a

micrograph of polished sections of a zirconia plasma sprayed coating. Both plan and section views were considered. Elastic properties were treated as orthotropic in the plane. Experimental measurements were performed *via* Hertzian indentation with a spherical indenter on an instrumented microhardness machine. The specimen area sampled for both the simulations and the experiments was approximately 0.01 mm^2.

Simulation studies were initiated to elucidate the influence of pore morphology and pore texture on average elastic behavior. Thus far, elastic properties of media containing a random distribution of elliptical pores of varying volume fractions were examined. Effective Young's moduli were found to be independent of the bulk Poisson's ratio, and effective Poisson's ratio were found to *flow* towards a common value at the percolation threshold.

Publications:

OOF (Object-Oriented Finite Elements), NIST Center for Theoretical and Computational Materials Science (CTCMS) software archives,

http://www.ctcms.nist.gov/~wcraig/oof/ and
http://www.ctcms.nist.gov/~wcraig/oof/manual/manual.html

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Processing/Microstructure Relationships

Principal Investigators: Andrew J. Allen and Gabrielle G. Long

Technical Objectives:

The objective of this research is to develop techniques for the microstructural analysis of plasma sprayed ceramic coatings, to characterize the anisotropic microstructure as a function of the spray process parameters, and to relate subsequent microstructural evolution to the service conditions.

Technical Description:

A combination of Porod small-angle neutron scattering (SANS) and multiple small-angle neutron scattering (MSANS) studies is revealing, and quantifying, the three void structures that govern the properties of plasma-sprayed ceramic coatings: anisotropic distributions of cracks within the splats and interlamellar pores between them, together with a wide size distribution of globular and large tetrahedral pores. The effects of several spray-process parameters and post-processing variables have been explored for both gray alumina and yttria-stabilized zirconia (YSZ), thick, self-standing, deposits. In addition, methods are being explored to extend some of these studies to thin deposits attached to substrates.

External Collaborations:

Hacene Boukari , University of Maryland, J. Ilavsky, Institute of Plasma Physics, Prague, C.C. Berndt and H. Herman, SUNY/Stony Brook, and A.N. Goland, Brookhaven National Laboratory are collaborating with the Ceramics Division on the processing-microstructural relationships.

Planned Outcome:

These studies will establish measurement techniques for quantative assessments of the microstructures of plasma sprayed ceramic coatings.

Accomplishments:

As a result of recent developments in the multiple small-angle scattering analysis, aimed specifically at the microstructural characterization of coatings, it has become possible to distinguish and quantify the intra-splat cracks, the inter-splat lamellar pores and the globular/tetrahedral pores. By combining this most recent enhancement of the MSANS method with anisotropic Porod scattering studies and with density measurements, the mean sizes, volume fractions, surface areas, and anisotropies, of these void systems have been deduced. Our experiments have established that a 1 h thermal treatment at 1100 °C or 1200 °C causes a significant reduction in the intra-splat crack porosity and

surface area, that some of this crack porosity seems to be converted partially into fine globular pores, but that the inter-splat lamellar porosity shows only a very modest decline until significantly higher annealing temperatures of 1300 °C to 1400 °C.

To explore these effects further, a high-temperature SANS furnace, previously designed and built for real time SANS studies of ceramic sintering, has been applied in real time studies of the effects of thermal treatment on YSZ ceramic deposits. The effects of varying the temperature and of aging at fixed temperature have been explored. The ramping experiments have shown that some annealing of the intra-splat crack system commences at temperatures only slightly above 600 °C, while the inter-splat lamellar pores do not anneal out significantly until the temperature is held above 1200°C. The aging experiment (at 1100°C) has shown an early increase in surface anisotropy (consistent with loss of intra-splat cracks), followed by a decrease due to some other process. The *ex situ* studies above suggest that partial conversion of the cracks to fine globular pores may be taking place, possibly leading to a dilution of the anisotropy as the globular pore fraction becomes more prominent with respect to the inter-splat lamellar porosity.

The implications of both of these sets of results, in modifying the anisotropies in the mechanical and thermal properties of thermal barrier coatings made from plasma-sprayed ceramic deposits, are significant, given that current jet and gas turbine operating temperatures are in the 1100 °C to 1200 °C range, with future applications likely to require higher temperatures.

The above studies are of thick, self-supporting, plasma sprayed ceramic deposits. To extend some of these methods to thin (< 200 μm) coatings on substrates, preliminary grazing incidence SANS experiments have been carried out. Using a grazing incident surface reflection geometry with the grazing angle just above the critical angle, it has been possible to recover surface area values and surface area anisotropies to within ~ 20% of those obtained by conventional SANS on the same materials. A mean depth sensitivity of 30 μm and a maximum depth sensitivity of ~ 150 μm have been established for this technique. These values are sufficiently small for studies of aeronautical or gas turbine coatings sprayed onto substrates.

Publications:

J. Ilavsky, G.G. Long, A.J. Allen, H. Herman and C.C. Berndt; "The Effect of Spray Distance and Chemistry on Pore and Crack Development in Plasma-Sprayed Ceramic Deposits," in Thermal Spray: Practical Solutions for Engineering Problems Ed. C.C. Berndt. ASM International, Materials Park, OH, pp 725-728 (1996).

J. Ilavsky, A.J. Allen, G.G. Long, S. Krueger, C.C. Berndt and H. Herman; "Influence of Spray Angle on the Porous Microstructure of Plasma-Sprayed Ceramic Deposits," J. Am. Ceram. Soc., 80, 733-742 (1997).

J. Ilavsky, A.J. Allen, G.G. Long, H. Herman and C.C. Berndt; "Characterization of the Closed Porosity in Plasma-Sprayed Alumina", J. Mater. Sci. 32, 3407-3410 (1997).

J. Ilavsky, G.G. Long, A.J. Allen, H. Herman and C.C. Berndt; "Changes in the Microstructure of Yttria-Stabilized Zirconia Deposits During Simulated Operational Conditions," Proc. 10th National Thermal Spray Conference (NTSC 10). Ed. C.C. Berndt. ASM International, Materials Park, OH. In press. (1997).

J. Ilavsky, G.G. Long, A.J. Allen, H. Herman and C.C. Berndt; "Use of Small-Angle Neutron Scattering for the Characterization of Anisotropic Structures Produced by Thermal Spraying," Silikatily (Czech journal). In press. (1997).

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Thermal Properties Measurements

Principle Investigators: Eduardo J. Gonzalez

Technical Objective:

This research is designed to identify those microstructural features in multilayer ceramic coatings that are important for thermal barrier applications. This study focuses on model coatings of Al_2O_3, ZrO_2 , and layered composites of ZrO_2/SiO_2 and ZrO_2/Al_2O_3 to identify relevant microstructural features that can help in the design of better and more efficient plasma spray coatings.

Technical Description:

Model ceramic coatings were prepared using a continuous dip coating technique developed at NIST. The process involves dipping a nickel base superalloy (Inconel 600, nominal chemical mass fraction composition: 76% Ni, 8% Fe, 16% Cr) substrate, 1 mm x 1.5 mm x 2.5 mm in dimensions, in an aqueous nitrate solution of the desired metal ion. The wet substrate is passed through a furnace held at a temperature between 500 °C and 1000 °C. In this part of the procedure, the solvent flashes off and the residual nitrate solution decomposes to hydroxide species. As the coated substrate reaches the hottest part of the furnace, the metal oxide forms and the oxide particles fuse to produce a solid metal oxide film. This procedure is repeated until the desired thickness is reached. After deposition, the coatings are heat treated using different experimental conditions to study microstructural changes.

The thermal properties of the coatings were studied using the photothermal deflection technique. This technique uses an intensity modulated argonion laser beam (4 mm to 6 mm in diameter) as a localized heating source on the surface of the sample. The modulated laser beam induces the formation and propagation of thermal waves in the sample. These thermal waves are also generated in the air near the surface of the sample. The thermal profile in this air volume near the surface of the sample is probed with a He-Ne laser that deflects off the sample's surface at a very shallow angle. A quad-cell photodiode position sensitive detector monitors the deflection of the He-Ne laser as it passes through the heated region. The beam deflection occurs because the index of refraction of the air in this region varies with the temperature profile. The vector components and the phase shift of the deflected beam as a function of position are recorded with the aid of a computer and evaluated with a multiparameter least squares fitting routine to calculate the thermal diffusivity of the sample. Since the thermal diffusion length can be controlled by adjusting the frequency of the heating laser, the sampling volume of material can also be controlled, and in principle can be reduced to a few micrometers provided that high modulation frequencies are used. This technique, therefore, has a high spacial resolution which makes it ideal for the characterization of coatings and thin films.

Planned Outcome:

This project will identify the microstructural features that significantly affect thermal transport in model ceramic coatings.

Accomplishments:

Coatings of α-Al_2O_3 , 4 μm to 6 μm thick, have been prepared using the continuous dip coating technique. The as-deposited films on an Inconel 600 substrate, are amorphous and exhibit a thermal diffusivity of (0.0033 ±0.0004) $cm^2\ s^{-1}$, a value comparable to window glass. Some of the coatings were crystallized by heat treating at 1000 °C for 3 h under flowing dry nitrogen gas. The thermal diffusivity of the films increased as they became more crystalline. However, during heat treatment, the porosity increased which limited their thermal diffusivity to (0.0219 ±0.0022) $cm^2\ s^{-1}$.

CERAMIC MACHINING

CERAMIC MACHINING

The Ceramic Machining Program was established in response to a comprehensive survey of the U.S. advanced ceramics industry indicating that the high cost of machining and, at times, uncertain reliability associated with machining damage are primary impediments to the widespread use of these materials. This program is designed to address generic industry needs related to measurement methods and standards in order to assist industry in the development of machining technology for the manufacture of reliable and cost-effective components made from advanced ceramics. The specific projects include: (1) effects of abrasive machining on mechanical properties of ceramics, (2) intelligent machining of ceramics, (3) chemical and chemomechanical effects of grinding fluids, and (4) abrasive finishing and wear of dental ceramics.

Ceramic materials studied in these projects include those ceramics intended for structural applications, such as silicon nitride, and the ceramics used for dental restorations, such as machinable glass-ceramics. The first two projects are conducted jointly with the 22 member Ceramic Machining Consortium with input from NIST's Precision Engineering Division, Statistical Engineering Division, and Standard Reference Data Program. The Consortium members, representing a broad spectrum of industry consisting of materials producers, machine tool builders, suppliers of expendables (such as grinding wheels and fluids), and end users participate by providing materials, testing, advice, and other in-kind contributions. The consortium members also provide input to the other two projects and assist NIST in formulating the scope of the research projects. The close working relationship developed between industry, academic institutions, and NIST not only ensures the relevance of the research projects but also promotes an efficient and timely transfer of research information to industry for implementation.

PROGRAM TITLE: Ceramic Machining

PROJECT TITLE: Abrasive Finishing and Wear of Dental Ceramics

Principal Investigator: Said Jahanmir

Technical Objectives:

The use of ceramics for dental restorations has been on a rapid rise in recent years due to their desirable aesthetics and durability. The conventional approach for preparing a ceramic restoration, for example a crown, consists of first taking an impression of the clinically prepared tooth, followed by preparation of a mold for casting. The cast crown is then shaped by grinding and polishing. As a final step, the dentist finishes the contacting surfaces with a dental handpiece to ensure a good fit. This sequence of events is time consuming and expensive. In a recently developed procedure, the dental restorations are prepared by machining instead of casting. Application of machining to ceramics, however, requires data and information on machinability as well as on the effects of machining on strength, wear resistance, and contact fatigue. Most premature clinical failures have been observed to result either from processing defects in the material, damage produced by machining, or from wear. The purpose of this research is to assess the influence of machining damage on strength and wear of dental ceramics.

Technical Description:

Abrasive machining by means of grinding with diamond tools is a process routinely used in dental laboratories for shaping of ceramic restorations and in dental clinics for tooth preparation and finishing of ceramic restorations. The surface and subsurface damage produced by the cutting action of diamond particles can be detrimental to the strength and clinical performance (e.g., wear) of restorations. The specific tasks during this reporting period consisted of evaluating the (1) Influence of Microstructure on Abrasive Finishing with Dental Handpiece, (2) Relationship Between Microstructure and Wear Resistance, and (3) Machining Damage in Enamel Associated with Clinical Tooth Preparation.

External Collaborations:

This project is an integral part of a larger program funded at the University of Medicine and Dentistry of New Jersey by the National Institute of Dental Research to evaluate the relationship between the microstructure of dental ceramics and their performance with respect to machinability, wear resistance, and mechanical properties. NIST Ceramics Division (S. Jahanmir) and MSEL (B. Lawn) are participating in this program together with the University of Maryland at College Park (Departments of Mechanical Engineering and Materials Science), the University of Maryland at Baltimore (Department of Restorative Dentistry), and the Naval Dental School (Department of Prosthodontics). In addition to the academic collaborators, three companies (Corning, Inc.; Vita Zhanfabrik; and Kurary) participate in this program by providing dental ceramics for the investigations.

The overall program of which this project is a part is unique as it brings together a diverse group of scientists and engineers with backgrounds in materials science, tribology, mechanical engineering, physics, chemistry, and dentistry. This group meets once a month to exchange information and plan future research activities. These meetings are highly beneficial for cross-fertilization of ideas and transfer of information between the different disciplines. The team members have been participating in workshops and conferences related to their respective fields of expertise as well as those outside their field for information exchange with their colleagues. In addition, the three international companies that provide materials for research receive the data and information generated in this program for their internal use in microstructural design of dental ceramics.

Planned Outcome:

This project will provide guidelines for microstructural design of dental ceramics to optimize performance based on wear of restoration and enamel, and guidelines for proper selection of machining parameters for use in abrasive finishing processes by dental technicians and dentists.

Accomplishments:

Evaluation of the damage produced by laboratory simulation of abrasive finishing process and tooth preparation by dentists in both teeth enamel and dental ceramics clearly suggest that (1) opposite to conventional belief, coarse diamond burs do not necessarily result in a high removal rate, (2) coarse burs produce a substantial amount of microcrack damage and chipping in enamel and dental ceramics, and (3) finer diamond burs must always be used to remove the damage that may have been produced by the use of coarse burs.

During this year, the abrasive finishing studies were focused on mica-containing glass ceramics used in dental restorative applications for crowns, bridges, and inlays. A series of glass-ceramics containing internally nucleated and crystallized mica platelets in a glass matrix was prepared by Corning for this study. The crystalline mica platelets ranged in diameter from approximately 1 μm to 15 μm. An instrumented finishing apparatus consisting of a dental handpiece was constructed and used for these studies. While the removal rate was found to increase with an increase in the mica platelet size, the extent of chipping fracture along the groove edges was found to decrease. In this study a comparison was made between coarse burs, which are often used for rapid removal of material from the surface of the tooth or restoration, and fine burs used for finishing. It was, however, found that the dental burs containing coarse diamond particles produced a smaller removal rate and more chipping damage, as well as rougher surfaces, than burs with fine diamond particles.

The subsurface damage in tooth enamel due to tooth preparation with diamond burs was evaluated using a recently developed technique for subsurface damage evaluation. The specimens were prepared by sectioning human third molars and cementing together highly polished sections. These "bonded-interface" specimens were machined, then separated, and the polished surfaces examined using both light microscopy and scanning electron microscopy. Four clinical diamond burs (coarse, medium, fine, and superfine) were used sequentially in a dental handpiece. Tooth preparation with the coarse diamond burs produced relatively large median type cracks in enamel. Finishing with fine

diamond burs was effective in crack removal. Therefore, the use of fine diamond burs must follow coarse burs to prevent premature fracture of teeth as a result of relatively large subsurface cracks produced by clinical tooth preparation.

Wear experiments were conducted at a low sliding speed with distilled water lubrication using a pin-on-disk tribometer. The test parameters (e.g., load, speed, sliding distance, etc.) were selected to simulate typical oral conditions. Examinations of the wear scars on the samples and of the wear debris using a scanning electron microscope indicated that wear of glass-ceramics was dominated by a microfracture mechanism initiated either along the cleavage planes or the weak mica-glass interfaces. As the size of the mica platelet increased, wear rate also increased. Since there exists a trade-off between machinability and wear performance, the microstructure (i.e., the size of the mica platelets) must be optimized to obtain restorations with a high machinability rating and at the same time a suitably high wear resistance. Wear experiments were also conducted on a series of composites containing glass particles in a polymeric matrix. The wear behavior of these materials was found to be very different from the glass ceramics, as tribochemical reactions between the glass particles and water was found to have a pronounced influence. The abrasive machining behavior of these composites, however, was controlled by a microfracture process, similar to the glass ceramics. Therefore, the relationship between machinability and wear of these composites was different from what was observed for the glass ceramics. This suggests that both microstructure and chemical composition of dental ceramics are important parameters for assessing the material's response to machining and wear.

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PROGRAM TITLE: Ceramic Machining

PROJECT TITLE: Chemical Effects of Machining

Principal Investigators: Stephen Hsu and Richard Gates

Technical Objectives:

The goal of this project is to understand the chemical interactions of coolants with diamond tools and work pieces so that a low cost machining technology can be developed.

Technical Description:

The project is studying the viability of using chemistry to enhance machining rate and to reduce surface defects while avoiding the use of modern ultra-stiff machining tools. The use of ceramics in industry has long been hindered from wide application due in part to the high cost of fabrication. Improved grinding fluid technology could lower the fabrication cost substantially.

The project surveys a wide variety of tribochemical reactions produced using a small bench top diamond cutter and an instrumented surface grinder. Test methods were developed to evaluate experimental grinding fluids in terms of the materials removal rates, surface finish, and amount of diamond worn during ceramic machining. Chemical kinetic experiments using thermogravimetric analysis and surface analysis were also performed.

External Collaborations:

In collaboration with Kennametal Inc., plant evaluations of grinding fluids are being conducted.

Accomplishments:

Several fluids were identified that can substantially increase silicon nitride machining rate. These substrates are environmentally friendly and non-toxic. The fluids were tested in a diamond cutter, a surface grinder, and a vertical grinder donated by Kennemetal. A fluid was developed and introduced at a manufacturing plant from March 1996 to August 1996. The fluid was used to machine cemented tungsten carbide cutting inserts using diamond wheels. The plant trial was successfully concluded after machining 170,000 inserts. The main benefit of the new fluid was to reduce the dressing frequency required to machine the parts to specifications. The maximum dressing cycle interval was increased from one dressing per 30 pieces machined to one dressing per 500 pieces machined.

The mechanisms leading to the improved dressing cycle were studied extensively during the last fiscal year. There are two contributing factors to the observed benefits. One is the nature and characteristics of the diamond used in the wheel manufacture. The other is the chemical

interaction between the diamond and the coolant. Under ceramic grinding conditions, molecules from the fluid adsorb onto the diamond surface forming a tenacious film which is hydrophobic. This film protects the diamond from oxidation and hydrolysis reactions. Thus the diamond particles remain sharp and protruded from the surface. However, different diamond particles have different oxidation and wear characteristics. Seven diamond powders were obtained from two diamond suppliers and tested for oxidation stability and wear. An electron spin resonance (ESR) technique was developed to characterize the impurity level and crystalline defects in the diamond. These characteristics were successfully correlated with oxidation rates measured from tests conducted in a thermogravimetric analyzer (500°C to 850°C).

Publications:

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PROGRAM TITLE: Ceramic Machining

PROJECT TITILE: Effects of Abrasive Machining on Mechanical Properties of Ceramics

Principal Investigators: Lewis Ives and Said Jahanmir

Technical Objectives:

Advanced ceramics are being increasingly used in automotive, aerospace, and manufacturing applications due to their excellent wear and corrosion resistance. Examples include cutting tools, valves, bearings, and seals. Although ceramics have attractive mechanical and chemical properties, high machining costs and sometimes an uncertain reliability due to machining damage are obstacles to more wide-spread use. The objective of this project is to assist industry in the development of machining technology for the manufacture of reliable and cost-effective components made from advanced ceramics. This project provides measurement methods and data to assess the influence of damage produced by high-rate machining on properties and performance of ceramics.

Technical Description:

Specific tasks during the reporting period consisted of the following: (1) Effects of Grinding on Strength of Silicon Nitride, (2) Influence of Finishing Methods on Strength and Contact Fatigue of Silicon Nitride, (3) Measurement of Inter- and Intra-Laboratory Strength Variations Associated with Grinding, and (4) Standard Test Method for Assessment of the Effects of Machining Damage on Strength. These tasks were carried out jointly with the members of the Ceramic Machining Consortium. The Consortium members provide in-kind contributions consisting of ceramic materials, diamond grinding wheels, sample preparation, testing, and input to the project direction.

External Collaborations:

Industrial and academic organizations participate in this project by joining the Ceramic Machining Consortium and signing a CRADA for joint research on specific research tasks. The following is a list of organizations that were members of the Consortium during the last year: Cabot Corp.; Ceradyne, Inc.; Cercom, Inc.; Chand Kare Technical Ceramics; Cincinnati Milacron, Inc.; Eaton Corporation; Ford Motor Company; General Electric Company; General Motors Corporation; Georgia Institute of Technology; Heraeus Amersil; Kansas State University; Landis / Western Atlas; Norton Company; Stevens Institute of Technology; Technology Assessment and Transfer, Inc.; Torrington Company; University of Delaware; University of Maryland; University of Massachusetts; University of Rochester; and West Advanced Ceramics, Inc.

The fifteen industrial members of the Ceramic Machining Consortium participate in joint research and have direct access to the data generated in this project. The results are being used by the member companies to develop new ceramic materials, improved grinding wheels, and grinding

fluids, and to optimize their manufacturing operations to develop cost-effective machining methods.

Planned Outcome:

Three major outcomes are expected from this program: (1) recommendations for optimum selection of grinding parameters to be used for specific silicon nitride ceramics, (2) guidelines on finishing methods to obtain damage-free nano-precision surfaces on bearing grade silicon nitride ceramics, and (3) recommended test procedures for the assessment of the effects of machining damage on strength.

Accomplishments:

The results of a comprehensive study on three types of silicon nitride showed no distinguishable change in fracture strength with different grinding conditions for the specimens ground parallel to the tensile direction of the flexure test bars. Specimens ground transverse to the tensile direction showed a substantial decrease in strength. Among the grinding parameters studied, wheel grit size had the greatest influence on strength. The strength of samples was lower when a wheel with coarse diamond grit was used for grinding. In this study flexure bars with rectangular cross-sections were prepared following the guidelines suggested in the ASTM standard C-1161. Since ceramic components used in many applications have a circular cross-section, a study was initiated to evaluate the effects of grinding on the strength of round bars. To accomplish this task, a new flexure fixture was designed and constructed. The new fixture was tested with fused silica glass samples. This fixture will be used to evaluate the effects of grinding on the strength of silicon nitride and zirconia specimens provided by Consortium members.

In the studies of the influence of grinding on flexure strength involving several Consortium members, relatively large variations, both within the laboratories and between the laboratories, were observed. A round robin exercise was, therefore, initiated to evaluate the source and the extent of these variations. Eight Consortium members are participating in this study. The results so far suggest that the processes of truing and dressing used to condition the diamond wheel prior to grinding have a major influence on strength variability observed in this study.

Discussions were initiated with the ASTM Committee (C-28) on Advanced Ceramics regarding the need for a standard test method for the assessment of the effects of machining on the strength of advanced ceramics. A new task group in C-28 has been formed to prepare a standard test method for this purpose. An outline of the proposed method was presented to the C-28 Committee and was approved. The proposed test method is based primarily on the procedures developed and evaluated jointly with the members of the Consortium during the past five years.

In connection with the investigation of the influence of machining damage on rolling contact fatigue, test samples of a hot-isostatically pressed silicon nitride were prepared and distributed to the participating Consortium members. Two finishing methods: chemomechanical polishing

(Stevens Institute of Technology), and conventional bearing superfinishing (Torrington) were used on the samples. The samples were characterized at NIST for surface roughness and form, and were sent to Torrington for rolling contact fatigue testing. The average roughness R_a of the samples finished by chemomechanical polishing was better than 0.004 μm, while the roughness on samples finished by conventional finishing was about 0.027 μm. Preliminary tests have shown a better performance for the samples finished by the chemomecahnical polishing method.

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PROGRAM TITLE: Ceramic Machining

PROJECT TITLE: Intelligent Machining of Ceramics

Principal Investigators: Said Jahanmir, Mario Cellarosi, and Tze-Jer Chuang

Technical Objectives:

The current practice of grinding, as applied to ceramics, is labor intensive and operator dependant. Since grinding can introduce surface and subsurface damage in the form of microcracks, residual stresses, and phase changes, operators take a conservative approach, using a "slow" grinding process, which further increases the cost of ceramic components. The objective of this project is to develop measurement methods, process models, and databases for in-process control and off-line optimization of ceramic grinding to minimize machining damage.

Technical Description:

Grinding, by definition, is a process where removal of material takes place at individual contacts made between the abrasive particles in the grinding wheel and the work piece. As the wheel engages the workpiece at a predetermined depth of cut (or down feed) each contact point is subjected to normal and tangential force components. Summation of all the force associated with the individual contact points gives the overall macroscopic grinding force that can be measured by an appropriately configured force transducer. The force exerted on the ceramic work piece by each abrasive particle affects the removal of material and the formation of machining damage. The specific activities in this project consist of (1) Process Models for Prediction of Surface and Subsurface Grinding Damage, (2) Neural-Network Analysis for In-Process Control of Ceramic Machining, and (3) Ceramic Machining Database.

External Collaborations:

This research is coordinated with the present activities of the NIST Ceramic Machining Consortium. The current membership of the consortium includes fifteen companies representing ceramics producers, machine tool manufacturers, grinding wheel and grinding fluid suppliers, and end users. In addition, seven universities participate in the consortium providing basic and fundamental research results. The neural network task is a joint project between NIST and N.A. Technologies Company through the NIST-SBIR Program.

Planned Outcome:

The expected outcome from this project is a methodology for the intelligent grinding of ceramics, consisting of a PC-based database containing data and information on machinability of advanced ceramics, sensors for monitoring the wheel topography and grinding forces, damage formation models for grinding with wheel topography and grinding forces as inputs, and strategies for on-

line modification of grinding parameters to minimize subsurface damage and the resultant low strength.

Accomplishments:

A two-dimensional finite element model was constructed to model the forces produced between the grinding wheel and the work piece in addition to the deformation field and stresses produced in the work piece. The input parameters for the model included both material properties and grinding parameters. The dimensions of the work piece model were selected so that its length in the horizontal direction was several times greater than the length of the cutting zone and that the distance into the work piece was at least ten times larger than the depth of cut. The boundary at the cutting zone was determined based on the wheel size and the velocity ratio. Loading was imposed by displacements in the cutting zone dictated by the local undeformed chip thickness, which is a function of grinding parameters. For a given set of input parameters, the model predicts the normal and tangential force components imposed by the grinding wheel. The deformation and the stress fields created in the work piece were calculated. The results indicated that, for a sintered reaction bonded silicon nitride, the high shear stresses in the cutting zone could control the mode of failure and result in the formation of microcracks and removal of material by a microfracture process. As expected, the size of the subsurface region subjected to high shear stresses increased with corresponding increase in the depth of cut. As a confirmation of the model, the forces on the work piece computed from the finite element model were compared to measured grinding forces; they were found to be equivalent.

During the past year the database effort was focused on collecting data from the open literature. Based on the availability of information and the requirements for certain types of parameters, a minimum set of required information was determined. After evaluating several hundred publications, about forty references were selected that met the minimum requirements. The data were then examined and verified for errors and inconsistent and/or duplicate data. The evaluated data collected from the literature and those obtained at NIST were compiled into the final version of the Ceramic Machinability Database. This database included about fifty-five fields of information applicable to ceramic grinding including material identification and properties, grinding parameters and conditions, process outputs and results, and references and comments. More than seven-hundred data records (i.e., rows of data) were included in the database. Two versions of the database (Microsoft Access and FoxPro) were distributed to the Consortium members.

The goal of the Phase I SBIR project contracted with N.A., Technologies is to demonstrate the feasibility of using neural network models for the analysis of ceramic machining data. The strength data collected jointly with the Consortium on three different silicon nitrides were sent to N.A. Technologies. A model was developed from these data using artificial neural systems with algorithms that were previously designed for other manufacturing applications. Plans in the next phase of this project call for the expansion of this model to include fusion of data with the data obtained directly from sensors during grinding (e.g., grinding forces, acoustic emissions, wheel topography).

CERAMIC PROCESSING

CERAMIC PROCESSING

Ceramic products are primarily produced by powder processing, where raw material powders are mixed with forming additives and shaped by various means into green bodies, which are then fired to the final, hardened state. The processing costs can vary greatly depending on the reproducibility and reliability of the process operation. One key to reliable and rapid development of new products is having good test methods to analyze the material at its different stages of processing. Unfortunately, no satisfactory measurements infrastructure yet exists within the ceramics industry, and as a result, much processing relies largely on art and experience.

The program on ceramic processing focuses on measurement methods of generic value to all ceramic companies. Clearer definitions are needed as to what needs to be measured, how is it to be measured, and how reliable is the measurement. Also, the value of the measurement to optimizing the processing operations is needed.

All subsequent operations depend on the raw materials characteristics, and therefore the measurement of the physical and chemical properties of powders is an important component of the program. The reliability of various measurement techniques is being assessed in a cooperative international program under the direction of the International Energy Agency and its subtask on ceramic powder characterization which is being coordinated at NIST in the ceramic processing program. In addition, SRMs needed to calibrate the measurement instruments in use are being developed. An intramural ATP project on the mechanism of drying, using NMR imaging, is in progress and is providing direct insight on the moisture gradients formed during drying.

A new consortium called the Ceramic Processing Characterization Consortium (CPCC) was formed in June, 1997. Its mission is to assist the U.S. ceramics industry in establishing a generic, powder processing measurements infrastructure. The goal is to assess the measurement needs in ceramics processing and to take all necessary and feasible actions to find viable solutions. Measurement procedures are generally nonproprietary, so ceramic companies can work together to improve the measurement methods of common interest and benefit. The members of the CPCC are volunteers, from companies, instrument makers, universities, and national laboratories. Their contributions to the projects of the CPCC should result in rapid advances in the near future. The current projects are: (1) powder characterization; (2) green body characterization; (3) moisture measurements; (4) dispersion and rheology; and (5) microstructure development. Teams for each of these projects have been formed. The reliability and reproducibility of commonly used instruments will be assessed, new methods will be developed, and a better understanding of how the measured properties affect the behavior of the material at different stages of processing will be developed through basic research studies. All studies will be generic and nonproprietary. All members of the CPCC share in the carrying out the work in the CPCC project teams.

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE : Ceramic Processing Characterization Consortium

Principal Investigator: George Onoda

Technical Objective:

The objective of this project is to establish a measurements infrastructure for the US ceramic processing industry. Such an infrastructure has the potential of benefiting a large segment of the ceramic industry by reducing processing costs and increasing product reliability.

Technical Description:

The Ceramic Processing Characterization Consortium (CPCC) was formed as a national consortium with members from the U.S. ceramic industry, instrument manufacturers, academia, and national research laboratories. The 85 current members represent 50 companies, 10 universities, and 5 government laboratories or agencies.

The CPCC serves to focus all of the activities in the Ceramic Processing Program. This consortium currently has four active CPCC projects: (1) Powder Characterization; (2) Dispersion and Rheology; (3) Green Body Characterization; (4) Moisture and Drying; and (5) Microstructure Development. The projects of the Ceramic Processing Program are integrated with the CPCC projects.

The industrial members of the CPCC help to prioritize the measurement needs in ceramic processing, which serves as a guide to design projects. All members of the CPCC have been encouraged to take an active part in contributing to these projects.

External Collaborations:

The external collaborators are the members of the CPCC. The members have a memorandum of understanding agreeing to free exchange and sharing of results and information obtained through the work of the consortium.

Planned Outcomes:

The planned outcomes for the consortium are:

(a) The close cooperation of all CPCC members in working together to create a common, measurements infrastructure.

(b) The implementation of improved measurement methods in companies, for both off-line and on-line monitoring.

(c) Successful research accomplishments that produce new measurement techniques for the ceramic processing industry.

Accomplishments:

The CPCC was formally established with a kickoff meeting on June 5-6, 1997. This meeting was attended by 55 persons. Of these, 25 were members and others were invited guests who wished to learn more about the CPCC. The basic policies of the CPCC were established. A lengthy discussion lead to the identification of the more important measurement needs of industry. These needs were grouped into five characterization projects: (a) Powders, (b) Green bodies, (c) Dispersion and rheology, (d) Moisture and drying, and (e) Microstructure development.

Research progress for four of the five projects have been initiated and preliminary studies have been conducted. Emphasis was given to determining measuring instruments for moisture content and green density that could potentially be used on line. A number of important instruments have been uncovered and are being evaluated. Work has also been started on creating a database for dispersing agents, NMR studies of the drying process, and evaluation of the accuracy of laboratory methods for measuring green density.

In July 1997, the first issue of the CPCC news bulletin CERAMIC MEASURES was published and distributed. This publication summarized the decisions and plans established at the kickoff meeting, as well as provided news relevant to measurements for ceramic processing.

Efforts to increase the membership of the CPCC have resulted in considerable success. Letters and the first issue of CERAMIC MEASURES were sent to top management in all of the ceramic companies in the U.S.

The second CPCC meeting has been organized and will be held in Gaithersburg, MD on December 15, 1997.

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE: IEA Subtask 10 (Secondary Powder Properties)

Principal Investigators: George Onoda and Lin-Sien Lum

Technical Objectives:

The objective of this project is to establish and refine pre-standards procedures for the characterization of primary and secondary properties of ceramic powders.

Technical Descriptions:

There are four focus areas in this international interlaboratory study: 1.state of dispersion of powders; 2. rheology of slurries; 3. properties of spray dried powders; 4. evaluation of green bodies. Three powders were studied: silicon nitride, silicon carbide, and aluminum oxide in both the as-received and spray dried granule form. This project is a continuation of the previous project (Subtask 8) where initial examination of different methods and instrumentation for the characterization of secondary properties were accomplished. Procedure improvements of selected methods were conducted for Subtask 10.

External Collaborations:

Technical collaborations with international organizations: BAM (Germany), Swedish Ceramic Institute (Sweden), VITO (Belgium), and JFCC (Japan).

Planned Outcomes:

This project will establish improved characterization procedures for the following secondary properties: deagglomeration of ceramic powders in slurries; rheological properties; flow rate, size distribution, moisture content, and binder content of spray dried powders; bulk density, porosity, and green strength of green body compacts.

Accomplishments:

A method to determine the state of dispersion of ceramic powders has been developed. The method involves following the changes in the particle size distribution as a function of the ultrasonication time used to disperse the powder in dilute suspension. If deagglomeration occurs by ultrasonication, then the particle size distribution should shift toward the finer size as the ultrasonication time is increased. The final dispersed state is the size distribution that is attained after no further changes in particle size distribution occur with longer ultrasonication time.

Measurement procedures have been developed to determine the rheology of ceramic suspensions using a rotational viscometer and a rotational rheometer. The suspensions in these procedures have a solids volume fraction of 30 % of powder. The procedures specify the measurement of apparent viscosity, shear-thinning index and thixotropic response in water-based ceramic powders slurries over a shear rate range of *ca* 1s to 500 s.

Preliminary procedures have been developed to determine the flow rate, size distribution, moisture content and binder content of spray dried powders. The procedure for flow rate measurement uses a modified Hall Flow method. A dry sieving technique is used to measure the size distribution of the granules. The moisture and binder content is determined by measuring the weight loss of the powders after drying.

Procedures to determine bulk density and porosity measurements on green body compacts have been developed. The bulk density is determined by measuring the external dimensions and the weight of the compacts. A mercury porosimetry technique is used to determine the porosity of the compacts.

Publications:

Final DOE report on Subtask 8, "Development and Testing of Primary and Secondary Properties of Ceramic Powders, Final Report, published in December, 1996.

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE: Moisture and Drying

Principal Investigators: Pu Sen Wang and George Onoda

Technical Objectives:

One objective of this project is to gain new insights on the mechanisms of drying of ceramic green bodies by applying nuclear magnetic resonance (NMR) spectroscopy and imaging (MRI).

Another objective is to bring about rapid technology transfer of recently developed moisture sensors that may be used in ceramic processing applications of interest to CPCC members.

Technical Description:

The drying mechanisms in green bodies are not completely understood because most past studies relied on weight loss curves to interpret the results. Little is known about how the physical and chemical states of water exist within a green body, and without this information, drying mechanisms are difficult if not impossible to postulate clearly. NMR spectroscopy can determine the physical and chemical states of water molecules. And with imaging, the moisture distribution and its changes during drying can be monitored.

A number of moisture sensors have emerged in recent years and have been used in some industries, such as wood processing and concrete. These have not yet been applied to the ceramics processing industry to any appreciable extent. Various sensors involve microwaves, nuclear magnetic resonance, near infrared, capacitance, *etc.*

External Collaborations:

The ATP external collaborators are AlliedSignal Ceramic Components (Torrance, California) and AlliedSignal Research Laboratories (Morristown, New Jersey).

In the CPCC studies, the collaboration team includes members from AlliedSignal, Hall China Co and Pfaltzgraff Co.

Planned Outcomes:

In the ATP intramural program, we expect to delineate, for the first time, a number of physical and chemical states of water in green bodies. Second, we expect to relate these states to the different stages of drying and to understand how changes in temperature affect the mechanisms. With this new understanding, our external collaborators will have guidelines to optimize the conditions of their drying process so as to produce an improved dry, green body.

In the CPCC moisture studies, we seek to have in-plant assessments of the newer moisture detectors and the eventual installation of sensors in ceramic processing lines.

Accomplishments:

We were able to distinguish a number of states of water in clay-based, green bodies based on their NMR spectra. The molecular freedom of water can be measured by the NMR resonance line width. The more strongly a water molecule is constrained by surrounding molecules, the narrower is the line width. The clay bodies were provided by a dinnerware company, a potential user of the AlliedSignal process developed in its ATP program. Using clay bodies saturated with water, the following states were identified:

(a) Free tumbling water: The line width is less than 500 Hz. Water in this state was detected only when large, macroscopic voids developed during drying.

(b) Loosely bound water: Most of the water molecules(~70% of the water) in this stoneware clay sample were loosely bound and had line widths ranging from 4000 Hz to 6000 Hz. We observed that water in this state was the first to evaporate, and followed a linear, 1st order rate. It is believed that this water exists in interconnected pore channels, where it could be drawn to the surface by capillary action and evaporated.

(c) Isolated, loosely bound, water: A second class of loosely bound water was observed from NMR spectroscopy. This water leaves the body much more slowly and is believed to exist when isolated pockets of water remain after the interconnectivity of the water ceases.

(d) Surface absorbed water: The last group of water molecules to leave the sample represents ~12% of the removable water. They are bound to the surface and are more rigid. The line width varies from 7000 Hz to 12000 Hz.

(e) Chemically bound water: These are hydroxyl ions that are part of the chemical structure (e.g. aluminum hydroxide) and cannot be removed at 105 °C. The line width is 17000 Hz to 18000 Hz.

The drying rates were typically proportional to the temperature, as expected from previous weight loss studies. An independent nuclear spin-spin relaxation study by spin-echo sequence also agreed well with these results.

Moisture sensors of various types have been identified and some of their manufacturers have joined the CPCC. This will facilitate the evaluation of these sensors in the laboratory and in plant environments.

Publications:

Pu Sen Wang, "Physical Characterization of Water Molecules and Water Distribution in Aqueous Injection Molding by Proton NMR," accepted by Journal of the American Ceramic Society.

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE: Standard Reference Materials

Principal Investigator: James F. Kelly

Technical Objectives:

The primary objective of this work is to develop and certify glass/ceramic powders as particle size distribution standards. A necessary adjunct to this certification is the development of sampling protocols and size measurement procedures.

Technical Description:

The initial work in the development of these Standard Reference Materials is the selection of a powder material with the desired chemical and physical characteristics. These characteristics include size, shape, durability, and reactivity. Industrial sources of powders are identified, test powders are evaluated, and production specifications are developed in cooperation with the powder manufacturer. Procedures have been developed for splitting and bottling of the powder to achieve the necessary level of sample to sample homogeneity. The instrumental techniques utilized for the particle size measurements include optical and scanning electron microscopy, laser diffraction, sieving, sedimentation, and electrical zone sensing. The primary techniques are the microscopies because of the direct calibration with NIST line standards.

Planned Outcomes:

Development is underway for the recertification of the 40 μm to 170 μm glass bead SRM 1004b, and for the new SRM 1021, which will extend the lower range of available glass sphere size distributions standards to 1 μm . The measurement of particle size distribution by laser diffraction is in progress for three zeolite powders. Reference materials for sieving of raw materials in the glass manufacturing industry are in preparation as sieving standards.

Accomplishments:

Spherical glass SRM's 1003b, 1004a, 1017b, 1018b, and 1019b, covering particle size ranges from 15 μm to 2400 μm, are now available to industrial laboratories and test facilities. A spray dried zirconia powder, SRM 1982, has been developed for particle size calibration use in the thermal spray industry. Several thousand units of these materials have been produced and certified for size distribution and homogeneity. Approximately 500 units per year of these size distribution standards are purchased by industry for use in their quality control test programs.

Publications:

SRM 1018b, Glass Beads-Particle Size Distributions, NIST Standard Reference Materials Program (1997)

SRM 1019b, Glass Beads-Particle Size Distributions, NIST Standard Reference Materials Program (1997)

SRM 1982, Zirconia Thermal Spray Powder-Particle Size Distribution, NIST Standard Reference Materials Program (1996).

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE: Ultrasonic Characterization of Ceramic Suspensions

Principal Investigators: Vincent A. Hackley

Technical Objectives:

The primary objectives of this project are (1) applications development of non-destructive ultrasonic techniques for ceramic fine-powder suspension characterization and process control, and (2) utilization of ultrasonic techniques as research tools in fundamental studies of ceramic dispersion chemistry.

Technical Description:

Finely dispersed multi-phase fluid systems, such as ceramic powder suspensions, may be found at some stage of many industrial processes, but the ability to analyze these complex materials in their natural, undiluted state is limited by particle concentration restrictions associated with most conventional measurement techniques. Light scattering methods, for instance, require optically dilute samples; a condition rarely fulfilled in industrially relevant systems. There is also a growing need to develop on-line monitoring capabilities to support intelligent processing goals in industry.

Ultrasound is non-destructive, non-invasive, and interacts much more weakly with dispersed matter compared to electromagnetic radiation. These properties are ideal for application to ceramic powder processing, where complex multicomponent mixtures at high solids concentrations are frequently encountered. There are three ultrasonic-based measurements which are available in our laboratory: electroacoustic, attenuation, and velocity. The electroacoustic technique is based upon the coupling between electric and acoustic fields in a suspension of charged particles. This technique can be used to measure both particle size and electrical charge in suspensions. Attenuation spectra are used to determine particle size distributions based on the characteristic extinction pattern of ultrasound in a suspension, and ultrasound velocity measurements may be used to determine particle concentration *in situ*.

External Collaborations:

Collaborative efforts continue with a researcher at Changwon National University, South Korea, to investigate surface chemistry of electronic ceramic powders for aqueous processing applications. A collaborative interaction was also initiated with a researcher from the University of Maryland to characterize and study the aqueous interfacial properties of bioceramic powders for applications in bone replacement and tooth restoration.

Planned Outcomes:

Four primary outcomes are expected: (1) development of the necessary measurement infrastructure (data, methodology) for the application of ultrasonic analysis in ceramic powder characterization and in sensors for active control of suspension-based processing; (2) improved understanding of component interactions during aqueous processing of complex, highly concentrated suspensions; (3) improved understanding of the physico-chemical behavior of dispersing agents used in ceramic powder processing; (4) generation of material-specific property data.

Accomplishments:

An international workshop on ultrasonic and dielectric characterization techniques for suspended particulates was held at NIST on August 4-6, 1997. The workshop was attended by 63 registered participants from 9 countries, including representatives from 18 industrial companies, 6 instrument manufacturers, 19 academic institutions, 2 national laboratories, and 1 foreign office of science and technology. The technical sessions consisted of 26 presentations emphasizing fundamental aspects, measurements in concentrated systems, instrument and sensor development, process control applications, and material applications. Proceedings will be published by the American Ceramic Society. A world wide web site was created to support workshop activities.

Testing and evaluation studies were carried out on a newly acquired ultrasonic spectrometer, the latest addition to the Ultrasonics Laboratory. This system measures the extinction and velocity of acoustic waves in particle suspensions over a frequency range from roughly 1 to 100 MHZ. The influence of particle size distribution, agglomeration, solids concentration, bulk material properties, and measurement parameters were examined. Measurements were performed at solids concentrations as high as 30% volume fraction, and in mixed-particulate suspensions containing two powder components.

Publications:

Hackley, V.A., "Colloidal Processing of Silicon Nitride with Poly(acrylic acid). I. Adsorption and Electrostatic Interactions," J. Am. Ceram. Soc., **80**, 2315 (1997).

Hackley, V.A., "Colloidal Processing of Silicon Nitride with Poly(acrylic acid). II. Rheological Properties," submitted to J. Am. Ceram. Soc. (1997).

Paik, U., Hackley, V.A., Choi, S., and Jung, Y., "The Effect of Electrostatic Repulsive Forces on the Stability of $BaTiO_3$ Particles Suspended in Non-Aqueous Media," to be published in Colloids Surf. A (1998).

Hackley, V.A., "Measuring Particle Size of Slurries with Sound Waves," Ceramic Industry, June issue, pp 52-56 (1997).

DENTAL AND MEDICAL MATERIALS

DENTAL AND MEDICAL MATERIALS

The Dental and Medical Materials Program provides basic materials science, engineering, test methods, and standards to sectors of the health-care industry for the development of new or improved materials and delivery systems. The focus of this program is the development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability.

Dental restorative composites are heterogeneous materials having three essential phases: (1) a polymeric matrix which comprises the continuous phase, (2) fillers of various types, sizes, shapes and morphologies which constitute the disperse phase and (3) an interfacial phase that, in varying degree, bonds the continuous and disperse phases into a unitary material rather than a simple admixture. While all three phases are important in determining the properties of the composites, this program is focused primarily on the interfacial and polymer matrix phases. Since the polymerization shrinkage that occurs in the matrix phase is one of the most commonly cited deficiencies of dental restorative composites, resources are allocated to develop high conversion, durable, low shrinkage polymeric materials for use in dental resin and composite applications. The polymeric matrix of a dental composite typically is formed by free radical polymerization of a resin which is one or more vinyl monomers, usually of the methacrylate class. Polymerization is started either by the formation of initiating radicals from chemical reduction-oxidation(redox) reactions or by photochemical redox reactions.

Although only a minor component of these composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler exerts a profound effect on the properties of the composites. Because these composites are used in an aggressive, aqueous environment that constantly challenges the vulnerable silane mediated polymer-filler bond, understanding of this critical interfacial phase is being acquired so that strategies can be developed for its improvement.

The occupational and environmental hazards associated with the use of mercury-containing dental alloys are a recurring source of public concern. Since dental amalgams have performed exceedingly well over more than one hundred years, the development of a direct filling material still based on the common constituents of dental amalgams, other than mercury, is desirable. This project is focused on acid-assisted consolidation of chemically precipitated silver powders and property measurements of hand consolidated test compacts prepared with the tools and procedures normally employed by dentists. The observed values of flexural strength for the silver compacts were equal or superior to mercury amalgams. Corrosion resistance, microleakage and marginal toughness values of the compacts were found to be superior to those of amalgams. Wear and biocompatibility studies on the hand consolidated compacts are in progress.

Dental research directions in support of the goals are established in collaboration with the American Dental Association(ADA), the National Institute of Dental Research (NDIR), and guest scientists from the U.S. Navy and the U.S. Public Health Service. NIST has hosted research associates from ADA since 1928. Currently, the ADA Health Foundation sponsors 32 research associates at NIST. The collaborative relationship between that professional association and the federal government is unique, and continues to develop and transfer important new technologies to dentistry and medicine.

PROJECT TITLE: Dental and Medical Materials

PROJECT TITLE: Wear Test Development for Total Joint Replacements

Principal Investigators: Stephen Hsu and John Tesk (Polymers Division)

Technical Objectives:

This project aims to develop an accelerated test method to effectively evaluate biomaterials used in total joint replacement.

Technical Description:

An industrial consortium was formed in October 1996 to develop an effective wear test for biomaterials. The consortium consists of six orthopedic companies whose major business is the supply of hip and knee joint replacement parts. Based on a survey of wear test methods currently used by the members of the consortium, it has been concluded that no wear test apparatus currently provides an adequate test of joint replacement parts. Consequently, the project has been directed to develop a new test apparatus and to use the new apparatus to establish an appropriate test method.

Planned Outcomes:

The anticipated outcomes are: 1) a wear test apparatus optimized for the evaluation of the wear characteristics of total joint replacement parts; 2) the development of a test procedure appropriate for the conditions of biomaterials in joint replacements.

Accomplishments:

A technology survey was completed and a confidential report was issued to the members of the consortium in March 1997. Current industrial test procedures from the consortium members were compiled and evaluated both theoretically and experimentally. All test procedures used pin on disk configurations, with variations in duration, wear criteria, motion (unidirectional or reciprocating), and loading conditions.

At a meeting with the consortium members, these procedures were discussed, and no single procedure was judged to be adequate for the purposes of the consortium. Based on NIST research as well as reports from other research groups, the development of a new tester which would be capable of multi-axial motion, load spikes, and programmable cycles was recommended.

The design of the prototype wear tester has been completed. The multi-directional, reciprocating motions will be provided by two linear sliders which are positioned orthogonal to one another. The loading patterns and cycles can be programmed using actuators. Procurement of the control components and fabrication of the parts have begun. Completion of the prototype wear tester is projected to be in the second quarter of FY98.

EVALUATED MATERIALS DATA

EVALUATED MATERIALS DATA

The objective of the Evaluated Materials Data Program is to develop and facilitate the use of evaluated databases for the materials science and engineering communities. Both research- and application-directed organizations require readily available evaluated data to take advantage of the large volume of materials information developed on public and private sponsored programs. This information, particularly numeric data, is available in an ever increasing number of publications published worldwide. The necessity to consolidate and allow rapid comparison of properties for product design and process development underlies the database projects.

Evaluated databases are developed in cooperation with the NIST Standard Reference Data Program Office and, often, coordinated with the activities of other laboratories and scientific/technical societies. Research consists of the compilation and evaluation of numeric data as well as recently initiated efforts directed at more effective distribution and use of data. Database activities reflect laboratory programs with scientific capabilities required for appropriate data evaluation.

Database projects in MSEL include:

- Phase Equilibria Diagrams (PED), conducted in cooperation with the American Ceramic Society;
- the Structural Ceramics Database (SCD), a compilation of evaluated mechanical and thermal data for nitrides, carbides, and oxides of interest to engineers and designers;
- a ceramic machinability database, developed by the Ceramic Machining Consortium (see Ceramic Machining Program);
- a high T_c superconductivity database developed in cooperation with the Japanese Agency for Industrial Science and Technology (see High Temperature Superconductivity Program);
- development and implementation of the STEP protocol for the exchange of materials data, under the auspices of the ISO 10313 activity;
- the NACE/NIST Corrosion Performance Database developed by NACE and the Metallurgy Division to provide a means to select structural alloys for corrosive applications; and
- the Crystal Data Center developed by the Center for Neutron Research which provides fundamental crystallographic data on inorganic materials.

PROGRAM TITLE: Evaluated Materials Data

PROJECT TITLE: Ceramics Division Informatics Web Site

Principal Investigator: Edwin F. Begley

Technical Objective:

The objective of this project is to establish a World Wide Web site for the research results of the NIST Ceramics Division.

Technical Description:

This project addresses the issues of on-line access to technical information which may exist, for example, in the diverse forms of numeric materials property databases, microstructural images, committee activities, and research reports. Major issues include:

- Can existing PC database structures be utilized efficiently on the Web?
- Can DOS and Windows interface logic be preserved and completely supported on the Web?
- Can output displays maintain their flexibility and robustness?

Most importantly,

- Can solutions for these questions be developed so that making additional databases available on the Web becomes an incremental task?

External Collaborations:

During fiscal year 1996, the Systems Integration for Manufacturing Applications Program (SIMA) funded initial development of WebHTS, a prototype World Wide Web version of the NIST High Temperature Superconducting (HTS) Materials Database. This task was designed to address on-line access to standard reference data which is a key SIMA program area for testbeds and technology transfer. In fiscal year 1997, renewed SIMA funding was used to complete WebHTS and to expand the testbed to include demonstrations of electronic collaboration and, also, the transfer of different types of technical information.

Planned Outcome:

The outcome of this project will be the development of a World Wide Web site that will serve as an effective means of disseminating information related to the research of the NIST Ceramics Division.

Accomplishments:

The initial implementation of the Ceramics Division's World Wide Web site was completed. Included in the initial site were searchable access to the NIST High Temperature Superconducting Materials Database, selected project results from the "Ultrasonic Characterization of Particulates, Technology and Applications Development" research program, and a guide to international materials databases with Web links (where available).

The HTS was developed originally in a PC format which is distributed by the NIST Standard Reference Data Program (Standard Reference Database #62). This database was developed to provide evaluated thermal, mechanical, and superconducting property data for oxide superconductors. Conversion of the PC database to a Web database involves a basic translation from the programming language appropriate to a PC to the language of the Web. Further, the translation should preserve the basic interactive process by which users find information in the database. The interactive process consists of constructing the search criteria on the user's computer, searching a database on the NIST computer, and then displaying the retrieved results on the user's computer. These tasks were accomplished using the display, hyperlink, and query form features of HTML Version 3.2, the language currently recommended for the Web by the World Wide Web Consortium, and the database functions of MS Internet Interactive Server 3.0 Internet Database Connector (MSIIS IDC), HTX server extensions, and SQL. WebHTS may be accessed *via* the home page of the Ceramics Division, at http://www.ceramics.nist.gov/.

A second project was initiated to investigate using the internet to provide a forum for electronic collaboration. As a first effort towards this goal, a Web site was established in conjunction with an international workshop on acoustic, electroacoustic, and dielectric measurements which was hosted at NIST in August 1997 by Dr. V. Hackley of the Ceramics Division. The Web site provided an excellent medium for announcing this meeting and for distributing information generated by the workshop such as manuscript titles and abstracts, an executive summary, and proceedings. Plans were also developed to use the site to distribute computational tools and application notes for electroacoustic measurements and to serve as a centralized repository of property data and measurement parameters to support users of acoustic-based techniques.

While the primary objective for the development of the Ceramics Division's Web site is to provide a rapid and efficient means to disseminate information about the Division's work, the site may also be used to facilitate ongoing efforts. For example, scientists and engineers often have indicated that it would be useful to have a directory that would assist them with locating computerized and non-computerized sources of materials information. The development of a Guide to International Materials Databases was initiated in response to this interest. In many cases, the Guide includes hyperlinks to data sources on the Web.

Publications:

Web Site of the NIST Ceramics Division, E. F. Begley, 1997, http://www.ceramics.nist.gov/ .

PROGRAM TITLE: Evaluated Materials Data

PROJECT TITLE: Data Evaluation Methodologies

Principal Investigator: Ronald G. Munro

Technical Objective:

The objective of this project is to provide data evaluation methodologies to enhance the quality and reliability of materials property data for advanced ceramics.

Technical Description:

The most persistent concern in the use of materials property data in industry is the reliability of the data. Despite the obvious need for reliable data, little has been done to establish procedures and standards tailored to data evaluation efforts. The objective of this project is to develop and promote the scientific basis for data evaluation and its practical application to materials property databases.

Planned Outcomes:

Data evaluation methodologies, including the use of data quality indicators and specific assessment procedures, will be established.

Accomplishments:

A hierarchial procedure for the determination of a data quality indicator for materials property data was established and published in an ASTM Special Technical Publication. A new approach to quantitative data assessment in which all the properties of a particular material specification are viewed collectively as a coherent, selfconsistent representation of the material has been developed. The new approach has been applied to a study of the properties of the superconductor Y:123 and to a study of one particular specification of α-alumina.

Publications:

Reference Relations for the Evaluation of the Materials Properties of Orthorhombic $YBa_2Cu_3O_x$ Superconductors, R. G. Munro and H. Chen, Journal of the American Ceramic Society, Vol. 79, pp. 603-608 (1996).

Dependence of the Critical Temperature on Atomic Structure in Orthorhombic $YBa_2Cu_3O_x$, H. Chen and R. G. Munro, Physical Review B, Vol. 53, pp. 12496-12501 (1996).

Effects of Oxidation on the Flaw-Limited Strengths of Brittle Materials, R. G. Munro, Journal of the American Ceramic Society, Vol. 80, No. 3, pp. 811-812 (1997).

Data Evaluation Methodology for High Temperature Superconductors, R. G. Munro and H. Chen,

Computerization and Networking of Materials Databases: Fifth Volume, ASTM STP 1311, edited by S. Nishijima and S. Iwata, American Society of Testing and Materials, 1997, pp. 198-210.

Evaluated Material Properties for a Sintered α-Alumina, R. G. Munro, Journal of the American Ceramic Society, Vol. 80, No. 8, pp. 1919-1928 (1997).

PROGRAM TITLE: Evaluated Materials Data

PROJECT TITLE: Phase Diagrams for Ceramists

Principal Investigator: Stephen Freiman and Mary Clevinger

Technical Objective:

The primary objective of this project is to deliver critically evaluated phase equilibria data to industrial and academic customers.

Technical Description:

The technical evaluation of the phase diagrams obtained from the literature is carried out under NIST supervision. The preparation of the evaluated diagrams for dissemination is carried out at NIST with direct collaboration of on-site personnel of the American Ceramic Society (ACerS). The ACerS personnel are primarily supported by funds raised by the Society from industry, academia, and individuals. The collaboration represents an over-60-year agreement with ACerS to provide evaluated phase diagrams for the ceramic industry. The phase diagrams are supplied either in printed form or in computerized versions, and are distributed through the ACerS.

External Collaborations:

American Ceramic Society Research Associates, Christina Cedeno, Thomas Green, Evans Hayward, and Nils Swanson, participated in the evaluation, computerization, and production of the phase diagram publications developed in this cooperative program. Dr. Robert Roth, Dr. Helen Ondik, and Mr. Howard McMurdie acted as consultants for various parts of the project.

Accomplishments:

During the past year the second edition of a monograph containing phase diagrams pertinent to high T_c superconducting materials was published. The first monograph on this subject was published by ACerS/NIST in 1993. This second monograph, edited by Dr. Terrell Vanderah, Dr. Robert Roth, and Mr. Howard McMurdie contains 533 new diagrams of importance to all of the major high T_c systems.

The second major area of activity has been on a monograph containing all known phase equilibria information relative to zirconium (Zr) and its compounds. This monograph, edited by Dr. Helen Ondik, will bring together new as well as previously published evaluated diagrams; it will also contain bibliographic references to publications containing phase equilibria data, but no diagrams. Publication of this volume is scheduled for February, 1998.

Also during this past year, effort was directed towards correcting and improving the CD-ROM containing all of the phase diagrams published through Volume 11. Corrected CD-ROM's were distributed to customers.

Finally, work was begun on Volume XIII of the series Phase Equilibria Diagrams. This volume, edited by Dr. Terrell Vanderah and Dr. Robert Roth, will contain phase diagrams pertinent to oxide systems. Publication is scheduled for February 1999.

Publications:

Volume 12, Phase Equilibria Diagrams, ed. by R. S. Roth, focusing on oxides, was completed and published in 1996. This compilation contains 443 commentaries and approximately 800 diagrams.

Phase Diagrams for High T_c Superconductors II, ed. by T.A. Vanderah, R.S. Roth, and H.F. McMurdie, Am. Ceram. Soc., Columbus, Ohio, 1997.

PROGRAM TITLE: Evaluated Materials Data

PROJECT TITLE: Structural Ceramics Database

Principal Investigators: Ronald G. Munro and Edwin F. Begley

Technical Objective:

The objective of this project is to provide evaluated data and database standards in order to advance the application and understanding of structural ceramics.

Technical Description:

This project is designed to facilitate technological advances in materials science by providing evaluated thermal, mechanical, and corrosion property data for the broad class of materials variously called advanced technical ceramics, structural ceramics, engineered ceramics, or fine ceramics.

External Collaborations:

The Russian Research Center for Standardization, Information, and Certification of Materials has provided property data for selected oxide and carbide structural ceramics from Russian sources that were either previously inaccessible to U. S. industry or available only in Russian language publications.

Planned Outcomes:

Evaluated data for the thermal, mechanical, and selected corrosion properties of structural ceramics will be established and made available in electronic (PC and internet) formats.

Accomplishments:

The data set and a new Windows(TM) interface for Version 3 of the NIST Standard Reference Database Number 30: Structural Ceramics have been approved by the Standard Reference Data Program. The new data set contains a broad range of thermal and mechanical property data for oxide, carbide, nitride, boride, and oxynitride materials, including such materials as alumina, mullite, zirconia, silicon carbide, boron carbide, silicon nitride, aluminum nitride, titanium diboride, and sialon.

Publications:

Evaluated Material Properties for a Sintered α-Alumina, R. G. Munro, Journal of the American Ceramic Society, Vol. 80, No. 8, pp. 1919-1928 (1997).

Material Specifications of Advanced Ceramics and Other Issues in the Use of Property Databases with Corrosion Analysis Models, R. G. Munro, ASTM Journal of Testing and Evaluation, Vol. 25, No. 3, pp. 349-353 (1997).

HIGH TEMPERATURE SUPERCONDUCTIVITY

HIGH TEMPERATURE SUPERCONDUCTIVITY

A significant program in high T_c superconductivity is being conducted in MSEL and other Laboratories at NIST. The primary focus of the MSEL program is on bulk superconducting materials for wire and magnet applications. In carrying out this program, researchers in MSEL work closely with their counterparts in other NIST Laboratories, and collaborators in U.S. industry, universities, and other National Laboratories.

The primary thrusts of the program are as follows:

- Phase equilibria - Work is being performed in close collaboration with the U.S. Department of Energy (DOE) and its national laboratories to provide the phase diagrams necessary for processing these unique ceramic materials. A prime objective is the development of the portions of the phase diagram for the Pb-Bi-Sr-Ca-Cu-O system relevant to production of the high T_c materials.

- Flux pinning - Use is made of a unique magneto-optical imaging facility to examine flux pinning in a variety of materials, with much of this work being conducted in collaboration with American Superconductor Corporation. In addition techniques for better interpretation of magnetic measurements are being developed. Structure and dynamics of flux lattices and melting phenomena, critical to applications, are investigated with small-angle neutron scattering techniques.

- Damage mechanisms - Work is being carried out under a joint CRADA (cooperative research and development agreement) with American Superconductor Corporation as part of the "Wire Development Group" which involves a number of DOE National Laboratories and the University of Wisconsin to elucidate the effects of strain on the loss of current in superconducting wires. The primary tool being employed is the use of microfocus radiography available at the NIST beamline at the Brookhaven National Laboratory.

- Database - A high temperature superconductor database has been developed in collaboration with the National Research Institute for Metals (NRIM) in Japan. The High Temperature Superconductor Database (HTSD) includes evaluated open-literature data on numerous physical, mechanical, and electrical properties of a variety of chemical systems. The first version of the database is now for sale by the Office of Standard Reference Data.

- Crystal structure - Thermal neutron scattering techniques and profile refinement analyses are being utilized to investigate crystal and magnetic structures, composition, dynamics and crystal chemical properties. This research is being carried out in collaboration with a number of industrial and university experts and researchers at National Laboratories.

PROGRAM TITLE: High Temperature Superconductivity

PROJECT TITLE: Characterization of Damage in High-Tc Superconductor Tape Induced by Tensile Stress

Principal Investigator: Richard Spal

Technical Objective:

In industrial applications, high-Tc superconductor tape may be subjected to significant tensile stress. The objective of this project is to characterize the resulting damage at high tensile strain, and to relate the damage to the accompanying decrease in current carrying capacity.

Technical Description:

Multifilamentary Bi2223/Ag tape, manufactured by American Superconductor Corporation (ASC), Watertown, MA, was longitudinally strained in tension up to 1.5%, and the resulting damage was progressively studied nondestructively by synchrotron radiation microradiography and current-voltage (I-V) measurements. The final state of damage was also studied (destructively) by optical and scanning electron microscopies. The microradiography was performed on NIST beamline X23A3 at NSLS, while the I-V measurements and optical and scanning microscopies were performed at ASC.

It is well known that strain above about 0.4% produces cracks in the superconductor filaments, and consequently reduces the critical current, although surprisingly not to zero. At 1.5% strain, for example, the reduction is about one order of magnitude. The existence of a critical current clearly implies that the filaments are not completely ruptured, but the mechanism which maintains connectivity in the brittle filaments at high strain is not understood.

External Collaborations:

This project was performed under a CRADA with ASC. Project results were presented triannually to the Wire Development Group, consisting of scientists from Argonne National Laboratory (ANL), ASC, Los Alamos National Laboratory (LANL), NIST, Oak Ridge National Laboratory (ORNL), and Univ. of Wisconsin.

Planned Outcomes:

Expected outcomes are a quantitative description of damage in multifilamentary tape at high tensile strain, and first time demonstrations of the utility of synchrotron radiation microradiography and I-V data analysis for nondestructive studies in this field.

Accomplishments:

The microradiographs show that cracks produced in filaments by longitudinal tensile stress are

concentrated in narrow bands, which run perpendicular to the tape (and stress) axis, and completely traverse the filaments. The strain in regions between the bands, determined by digital analysis of pre- and post-strain microradiographs, is less than 0.4%, which is consistent with the absence of cracks in these regions. SEM micrographs of longitudinal sections and etched faces of tape show cracks which terminate before reaching the filament-matrix interface, demonstrating connectivity in damaged regions.

The connectivity of the damaged filaments was studied by analysis of the I-V data, using an electrical model which considers the division of current between the filaments and the metal matrix in the vicinity of cracks. In undamaged tape, practically all the current flows in the filaments. As cracks form and grow, current is increasingly diverted into the matrix, producing greater voltage for the same current. The physical quantities included in the model are: filament and matrix dimensions, strain, crack density, crack gap, current-carrying cross-sectional area of filaments in damaged regions, functional dependence of electric field on current density in the ab-plane of Bi2223, c-axis critical current density of Bi2223, and resistivities of the matrix and filament-matrix interface.

The I-V data were analyzed by fitting them to predictions of the electrical model using the method of non-linear least squares. Values for all but three of the physical quantities in the model were obtained directly from experiment or published data. For example, the functional dependence of electric field on current density in the ab-plane of Bi2223 was obtained from I-V data at zero strain, and the crack gap was obtained from SEM micrographs. The remaining three unknown quantities (current-carrying cross-sectional area of filaments in damaged regions, c-axis critical current density of Bi2223, and resistivity of the filament-matrix interface) were determined by the fitting procedure, which yielded physically reasonable values in all cases. For example, the value obtained for the c-axis critical current density of Bi2223 is comparable to that which has been reported for Bi2212 (no values have been reported for Bi2223). Due to the random nature of fracture phenomena, the current-carrying cross-sectional area will vary in different damaged regions, and thus is really a distributed quantity rather than a single value. Interestingly, the data could only be fitted without systematic error when this quantity was allowed to be distributed, demonstrating that I-V data is sensitive not only to the average value of the current-carrying cross-sectional area, but also to its distribution.

In summary, a detailed and consistent characterization of the damage produced in Bi2223/Ag tape by longitudinal tensile stress has emerged from the combined results of microradiography, microscopy, and I-V measurements.

Publications:

"Synchrotron Radiation Digital Microradiography of Strained High Temperature Superconductor Composite Tape," R.D. Spal, C.K. Chiang, G.N. Riley, and C.J. Christopherson, Proceedings of ICCE/4 Fourth International Conference on Composites Engineering, July 6-12 1997, Kohala Coast, HI, p. 935-6.

PROGRAM TITLE: High Temperature Superconductivity

PROJECT TITLE: Magnetooptic Imaging of High T_c Superconductors

Principal Investigators: Debra Kaiser and Marina Turchinskaya

Technical Objective:

The objective of this research is the development of a new tool that can be used to evaluate the magnetic flux distribution in high T_c materials.

Technical Description:

High T_c superconductors are currently being developed for a variety of power applications, all of which require high critical current density, J_c. The two major factors that influence J_c are the presence of weak links, which are regions of weakly superconducting material, and flux pinning centers, which are microstructural features that anchor magnetic flux lines. Both weak links and flux pinning centers can be evaluated by magneto-optic imaging, a technique that was originally conceived at the Russian Academy of Sciences and has been further developed at NIST. This technique provides a direct visualization of real-time magnetic flux flow in a superconducting material, thereby permitting correlation of flux flow with microstructure. Recent imaging studies on $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (BSCCO) /Ag composites, one of the leading materials for power applications, have provided considerable insight into the current limiting and flux pinning mechanisms in these important materials.

External Collaborations:

This research is conducted as part of the Wire Development Group, which provides the BSCCO/Ag composites for the magneto-optic imaging measurements.

Planned Outcome:

This research will provide producers and users of high T_c materials with a diagnostic tool to evaluate magnetic flux flow in their materials. The magnetic flux pattern is a direct indicator of the uniformity of current flow.

Accomplishments:

During the past year, magneto-optic imaging has been used to evaluate multifilamentary BSCCO/Ag composites with different architectures (i.e., number, size, morphology and arrangement of BSCCO filaments in the Ag matrix) in order to provide producers with some guidelines for designing composite structures that promote homogeneous magnetic flux distributions. Nine tape specimens with different architectures were examined nondestructively, wherein the magneto-optically active indicator film was overlaid directly on the unpolished tape surface. The upper layer filaments in the specimens were imaged through the outer silver sheath, and the homogeneity of the magnetic flux

distributions were assessed by converting the resulting light intensity maps into magnetic induction profiles and maps. The filament architecture had a strong effect on the homogeneity of the flux distribution in the upper layer filaments. Specimens containing 85 filaments arranged in closely spaced layers (spacing $d_{i, I+1}$ = 3 μm to 12 μm), or 8 filaments arranged in two widely spaced layers (d_{12} = 60 μm to 70 μm), had homogeneous flux distributions. In contrast, 16 filament specimens with closely spaced upper and second layers (d_{12} = 5 μm to 10 μm) that were separated from the third layer by a much larger distance (d_{23} = 50 μm to 60 μm) had localized inhomogeneities in the flux distribution that were correlated with gaps between the second layer filaments. Another source of inhomogeneity observed in a 5 filament specimen was localized reductions in filament thickness.

The magneto-optic images also revealed that the filaments in all of the specimens were well aligned. For specimens containing twisted filaments, it was possible to calculate the twist pitch directly from the images; the calculated values agreed well with those set by the processing equipment. These results demonstrate that magneto-optic imaging is a valuable nondestructive tool for evaluating commercially important characteristics of high temperature superconducting materials.

Publications:

"Effect of filament architecture on magnetic flux distributions in multifilamentary $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ /Ag composites," Debra L. Kaiser, Marina Turchinskaya, Gilbert N. Riley, Jr., and Craig Christopherson, J. Mater. Res. **12**, 1 (1997).

PROGRAM TITLE: High Temperature Superconductivity

PROJECT TITLE: Materials Property Database for High Temperature Superconductors

Principal Investigators: Ronald G. Munro and Edwin F. Begley

Technical Objective:

The objectives of this project are to provide evaluated data and database standards to advance the application and understanding of high temperature superconductors.

Technical Description:

This project is designed to facilitate technological advances in materials science by providing evaluated property data for thermal and mechanical properties and the principal superconductor characteristics for the broad class of materials commonly called high temperature superconductors or high-T_c materials.

External Collaborations:

The National Research Institute for Metals (Japan) is collaborating with NIST through a formal agreement to exchange property data on high-T_c materials. The NIST Ceramics Division is also collaborating with the intramural effort at NIST, Systems Integration for Manufacturing Applications (SIMA), to develop high performance computing and communication technology.

Planned Outcomes:

Evaluated data for the thermal and mechanical properties and the superconducting characteristics of high-T_c materials will be established and made available in electronic (PC and internet) formats.

Accomplishments:

Version 2 of the PC database, NIST Standard Reference Database 62: High Temperature Superconductors, was approved for distribution by the SRD program. This version contains data for cuprate, bismuthate, and the relatively new borocarbide superconductors. This version also includes data provided by a unique Japanese study of high-T_c superconductors, primarily of the Bi(Pb)-Sr-Ca-Cu-O family. The first internet version of the HTS database, WebHTS, was completed and made accessible *via* the Ceramics Division's home page at http://www.ceramics.nist.gov. WebHTS currently contains all the data from Version 1.0 of the PC database.

Publications:

NIST Standard Reference Database Number 62: High Temperature Superconductors, Version 2, R. G. Munro and E. F. Begley, Standard Reference Data Program, NIST.

Data Evaluation Methodology for High Temperature Superconductors, R. G. Munro and H. Chen, Computerization and Networking of Materials Databases: Fifth Volume, ASTM STP 1311, edited by S. Nishijima and S. Iwata, American Society of Testing and Materials, 1997, pp. 198-210.

WebHTS, E. F. Begley and R. G. Munro, 1997, World Wide Web, *via* http://www.ceramics.nist.gov.

PROGRAM TITLE: High Temperature Superconductivity

PROJECT TITLE: Phase Equilibria Relations in High T_c Superconductors

Principal Investigator: Terrell A. Vanderah, Winnie Wong-Ng and Lawrence P. Cook

Technical Objectives:

Experimental phase equilibria studies of superconducting materials are conducted with an emphasis on phase regions pertinent to the production of high-T_c wires. The project provides "processing map" information needed to improve the synthesis of higher quality (purity, texture) superconducting bulk materials for applications such as wires.

Technical Description:

Phase equilibria studies of the complex four-, five-, and even higher-component high temperature superconducting oxides are focussed on selected regions and conditions (T,P) pertinent to the manufacture of bulk conductors (wires, tapes). The successful processing of wires with high current carrying capacities and excellent superconducting properties is now known to require the *in situ* coexistence of high quality superconducting solid plus a liquid phase; the superconducting solid must be both pure in phase and textured in structure to eliminate weak links. The phase diagram work is therefore directed toward determining the location in composition-P-T space of the primary crystallization fields of the Bi(Pb)-Sr-Ca-Cu-O (BiSCCO) superconductors; that is, the regions where only 2 phases are present - the superconducting solid plus a liquid. Efforts this year have concentrated on the Pb-2223 (T_c ~ 110 K) BiSCCO superconductor in an ambient pressure atmosphere of 7.5% oxygen.

External Collaborations:

This project is supported in part by the DOE Superconductivity Program for Electric Systems which emphasizes development of bulk conductors; participants include government, academic, and industrial laboratories. NIST staff also interact and collaborate with LANL, ORNL, and ANL to combine complementary efforts, minimize duplication, and facilitate exchange of information as soon as it is available. For example, LANL staff working on wire manufacturing methods are now providing NIST staff with pertinent starting composition data so that NIST can determine experimentally the primary phase fields of the LANL composition.

Planned Outcomes:

Experimentally determined phase diagrams will be constructed to map out the primary crystallization field of the BiSCCO Pb-2223 (T_c ~ 110 K) phase together with the 2212 (T_c ~ 90 K) phase. This represents a technically important portion of the Pb-2223 primary crystallization field as it locates in temperature/composition space the coexistence of the two superconducting solids with liquid. In addition, this work will necessarily produce extensive phase equilibrium information on the subsolidus and subliquidus relations in which the superconducting phases participate; namely, solid-

state homogeneity regions and melting relations. The existence of this data will allow manufacturers to optimize starting compositions and processing conditions.

Accomplishments:

The primary crystallization field of the five-component BiSCCO Pb-2223 high temperature superconducting system has been determined in an atmosphere of 7.5% oxygen. The approximate outline of the primary phase field was located by first determining the subsolidus phase relationships involving the Pb-2223 superconductor at 810°C to 820°C under 7.5% O_2 (92.5% Ar) – an atmosphere chosen to approximate the conditions during the powder-in-tube processing method used by industry. A total of 11 phases were found to exist in equilibrium with the Pb-2223 phase. Sixteen five-phase equilibrium assemblages that included the 2212 superconductor (T_c ~ 90 K) together with Pb-2223 were found. These assemblages defined a multicomponent compositional space corresponding to the (Pb-2223 + 2212) solid-state compatibility region. Using this subsolidus data as a basis, the portion of the Pb-2223 primary crystallization field which included the 2212 superconductor was determined by measuring the melting temperatures and chemical compositions of the first liquids to appear from each of the five-phase subsolidus equilibrium assemblages. These data defined the limits of the Pb-2223 crystallization field in equilibrium with 2212. A multidimensional surface was fitted to the data, and in order to facilitate usage of the complex data, graphical representations were constructed by projecting through the 2212 phase into four-component space.

Publications:

Terrell A. Vanderah, Robert S. Roth, and Howard F. McMurdie, Eds.; "Phase Diagrams for High T_c Superconductors II", The American Ceramic Society, Westerville, Ohio, 1997.

W. Wong-Ng, L.P. Cook, F. Jiang, W. Greenwood, U. Balachrandran, and M. Lanagan, "Subsolidus Phase Equilibria of High-T_c Pb-2223 Superconductor in the (Bi,Pb)-Sr-Ca-Cu-O System under 7.5% O2," J. Mater. Res., in press (1997).

L.P. Cook and W. Wong-Ng, "Primary Crystallization Volume of BSCCO 2212: Applications to Crystal Growth and Melt Processing," submitted to Proc. Am. Ceram. Soc. Meeting, Cincinnati, Ohio (1997), in press.

W. Wong-Ng, L.P. Cook, W. Greenwood, U. Balachrandran, and M. Lanagan, "Preliminary Melting Data on Pb-2223 ([Bi:Pb]-Sr-Ca-Cu) Phase Under 7.5% O_2," Proc. Am. Ceram. Soc. Meeting, Cincinnati, Ohio (1997), in press.

W. Wong-Ng, "Crystal Structures and Crystal Chemistry of Bi-Containing Compounds in the Bi-Sr-Ca-Cu-O System," (book chapter), Nova Publishers, NY, in press.

W. Wong-Ng, L.P. Cook, and W. Greenwood, "Melting of $Sr_{14}Cu_{24}O_{24}$ at Various Oxygen Pressures," submitted to Physica C (1997).

C. Park, W. Wong-Ng, L.P. Cook, R.L. Snyder, P.V.P.S.S. Sastry and A.R. West, "Melting Investigation of $Bi_2Sr_{1.9}Ca_{2.1}Cu_3O_{10+x}$ by High Temperature X-ray Diffraction and Quenching", in preparation for Physica C.

W. Wong-Ng, L.P. Cook, and F. Jiang, "The Primary Crystallization Phase Field of "2212" Phase and the Effect of Ag Addition," in preparation for J. Am. Ceram. Soc.

MAGNETIC MATERIALS

MAGNETIC MATERIALS

Magnetic materials are pervasive throughout our society. They are used, for instance, in magnetic recording media and devices, in all motors, in all transformers, on credit cards, as permanent magnets, as magnetic sensors, on checks, in theft control devices, in automotive and small engine timing devices, in xerographic copiers, in magnetic resonance imaging (MRI) machines, in microwave communications, in magnetic separation, and in magnetic cooling. Magnetic materials include metals, ceramics and polymers at different size scales ranging from large castings to particulates, thin films, multilayers and nanocomposites.

In the present trend to make devices smaller, thereby reducing weight or increasing storage density, new magnetic materials are constantly being developed. One critical need for implementation of these materials is the development of the measurement science needed for their characterization, in terms of both material properties and performance. This is the focus of the Magnetic Materials Program. Proper measurements of key magnetic properties, determination of the fundamental science behind the magnetic behavior of these new materials, analysis of the durability and performance of magnetic devices and development of standard reference materials are key elements of this program. Some information is only obtainable by the use of unique measurement tools at NIST like the NBS reactor, or the magneto-optic indicator film apparatus for observation of magnetic domain motion. Of particular interest is understanding the magnetic behavior of low dimensional systems, in which one or more characteristic dimensions have been reduced to nanometer sizes. For these new materials, however, it is not known whether their exciting novel behavior is due to new physics or to a logical extension of large-size behavior to small dimensions. Consequently, implementation of this new type of material into marketable products is significantly delayed. NIST is providing the measurement science to address this critical unknown.

Areas of present study include the following:

- processing of magnetic multilayers for optimal giant magnetoresistance effect
- observation and micromagnetic modeling of magnetic domains for understanding magnetization statics and dynamics in advanced and conventional materials
- measurement and characterization of nanoscale magnetic interactions in multilayers, nanocomposites, and low-dimensional systems, needed for understanding and applying the physics of these materials
- measurement and modeling of the enhanced magnetocaloric effect in nanocomposites
- structure and magnetic characterization of new superconducting materials
- nanotribology of magnetic hard disks, measurement of stiction, friction, and wear at the nanometer scale

- measurement and understanding the origin of magnetic exchange bias in conventional and advanced magnetic structures and devices

- development of magnetic sensors of mechanical properties for incorporation as *in situ* controls in a steel mill

- development of a measurement system for the preparation of an absolute magnetic moment standard

By experimentally addressing important issues in magnetism, by bringing together the industrial and scientific communities through the organization of workshops and conferences in the area, and by the development and preparation of appropriate standards, NIST acts to accelerate the utilization of advanced magnetic materials by the industrial sector, and to enable industry to take advantage of new discoveries and innovations. In addition, close linkage with the national storage industry consortium (NSIC) which consists of 38 companies and a score of universities allows industrial relevance and partnership. Additional collaborations with Xerox, General Motors, Hewlett Packard, IBM, Seagate, and Motorola Corporations, for example, enable NIST to leverage its activities with the much larger, but complementary, capabilities of other organizations.

PROGRAM TITLE: Magnetic Materials

PROJECT TITLE: X-Ray Adsorption Studies

Principal Investigators: Daniel A. Fischer and Stephen M. Hsu

Technical Objectives:

The objective of this project is to determine the molecular scale structure and bonding characteristics of lubricating films deposited on hard disk magnetic media.

Technical Description:

As a part of the National Storage Industry Consortium (NSIC), NIST, Dow, and IBM are studying the interactions of lubricants with carbon hardcoat surfaces typical of a magnetic hard disk. The lubricants are cyclophosphasene (X-1P) and Fomblin (ZDOL). The following systems are being studied: ZDOL alone, X-1P alone, ZDOL/X-1P mixtures, and carbon overcoats (7.5 nm) with varying hydrogen (CH_x) and nitrogen (CN_x) contents. Near edge x-ray adsorption fine structure (NEXAFS) is used to probe the reactivity and orientation of the lubricants on the surfaces.

NEXAFS measurements have both elemental and chemically sensitivity, and are very sensitive to bond type. The technique can also be used to make direct comparisons between the surface and the bulk structures by measuring the simultaneous electron yield (10 nm depth sensitivity) and fluorescence yield (200 nm) spectra. In addition, the average orientation of chemical bonds can be determined from the polarization anisotropy of the soft x-ray absorption spectra.

External Collaborators:

Benjamin M. DeKoven (Dow), Donald J. Perettie (Dow), Gregg E. Potter (Dow), Timm Richardson (Dow), Singh Bhatia (IBM), and Ted A. Morgan (Dow).

Planned Outcomes:

Molecular orientation and bonding characteristics of lubricant molecules at lubricant/hard disk interfaces will be determined for selected lubricants and hard disk coatings.

Accomplishments:

Sixteen (16) combinations of lubricant and carbon hardcoat surface compositions have been studied. The orientation of the lubricants, their film thicknesses, and the compositions of the carbon hardcoat and magnetic media interfaces were determined. It was also possible to examine the lubricant/carbon hardcoat interfaces. The results indicate the formation of unsaturated carbon (pi*) bonding to carbon hardcoats as well as orientation/complexing in some cases. Changes in the Co in the buried surbsurface magnetic media layer upon lubricant chemisorption suggest that the lubricant may have penetrated the carbon overcoat.

Publications:

B. M. DeKoven, D. A. Fischer, G. E. Potter, D. J. Perettie, S. Bhatia, T. A. Morgan, and S. M. Hsu, "Chemistry/Orientation of Lubricants on Hard Disk Magnetic Media Substrates Using Near Edge X-ray Adsorption Fine Structure," submitted to the Journal of Vacuum Science and Technology A.

PROGRAM TITLE: Magnetic Materials

PROJECT TITLE: Wear and Lubrication Studies

Principal Investigators: Stephen M. Hsu, Richard S. Gates, Patricia A. McGuiggan, and Daniel A. Fischer

Technical Objectives:

The project focuses on the concepts and measurements of lubrication and wear in magnetic hard disk systems with a focus on improving the durability of the systems and possibly facilitating the development of a higher density data storage technology.

Technical Description:

The development of higher density magnetic storage disks requires the use of mechanical components capable of operating over regions of progressively smaller dimensions. Thin lubricating films are critical to the success of such systems, and measurement techniques probing progressively smaller scales must be developed to study these systems. These measurements are difficult to conduct and the phenomena are difficult to analyze because of the small size scale.

Working in conjunction with the National Storage Industry Consortium (NSIC) Tribology Working Group, we are developing new and novel concepts in protecting the magnetic hard disk surface *via* organized molecular film structures. Various monomolecular films are deposited on ultra-smooth disks over different carbon overcoat materials. Some of the disks are evaluated by industrial collaborators using component testing. Some of the disks are evaluated using the unique facilities at NIST. Surface characterization techniques are being developed to measure molecular orientation, film thickness, and surface bonding strengths. Fundamental measurements of surface forces, film strength, and nano-mechanical properties are also being studied to support the technological development effort by U.S. industries.

Planned Outcomes:

In conjunction with the information technology industry, this project will: (1) develop laboratory test procedures to evaluate the wear and lubrication characteristics of magnetic hard disk systems, (2) establish a model of how monomolecular films interact and protect the magnetic disks, and (3) determine relationships between thin film structures and their mechanical properties.

Accomplishments:

Experiments were done on a model system as well as on actual magnetic data storage disks. Stearic acid monolayer and submonolayer films were deposited on a copper surface and examined using Fourier transform infrared spectroscopy, time-resolved Raman spectroscopy, and ultra-soft x-ray absorption spectroscopy. The combination of these techniques allows the determination of the molecular orientation, inclined angle, and the nature of the bonding of the stearic acid with the

surface. These molecular parameters were correlated with the friction and wear performance of the model system to elucidate surface protection mechanisms. The stearic acid/copper system has been extensively studied before and therefore provides a calibration baseline for the techniques developed.

Various organic monolayers and monomolecular films were deposited on the NSIC CH_x coated surfaces as well as the CN_x coated surfaces. The coated disks were evaluated for friction and durability studies both at NSIC and NIST. Some films were found to perform much better than the current commercial practice.

Measurement techniques were also developed to measure thin film properties using an atomic force microscope, a nanoindenter, a nano-scratch tester, and a ball-on-inclined plane apparatus designed and built at NIST. During the last fiscal year, four measurement techniques were developed. A constant start and stop test technique for the super-smooth disks; a spin stand inclined plane sliding test method capable of measuring the durability of monolayer films; a reciprocating high speed test; and a test technique using a micrometer sized ball glued to an atomic force microscope tip to measure friction at the nanometer scale.

Publications:

S. M. Hsu, and X-H. Zhang, "Lubrication: Traditional to Nano-scale Films," Invited Chapter, in 'Micro/Nanotribology and its Applications' Edited by B. Bhushan, p. 399-414, Kluwer Academic Publishers, 1997.

D. A. Fischer, Z. S. Hu, and S. M. Hsu, "Tribochemical and Thermochemical Reactions of Stearic Acid on Copper Surfaces in Air as Measured by Ultra-soft X-ray Absorption Spectroscopy," Tribology Letters, **3**, 35-40 (1997).

D. A. Fischer, Z. S. Hu, and S. M. Hsu, "Molecular Orientation and Bonding of Monolayer Stearic Acid on a Copper Surface Prepared in Air," Tribology Letters, **3**, 41-45 (1997).

S. M. Hsu, "Boundary Lubrication: Current Understanding,", Tribology Letters, **3**, 1-11 (1997).

S. M. Hsu, F. Yin, J. Zhang, K. Zhang, and G. Bartelt, "Mono-molecular Layer Lubrication of Surfaces," to be published by in the Proceeding of Nanotribology for MEMs, Kluwer Academic Publishers, 1998.

MECHANICAL PROPERTIES OF BRITTLE MATERIALS

MECHANICAL PROPERTIES OF BRITTLE MATERIALS

Mechanical properties are the source of the greatest benefits as well as the most severe limitations of ceramic materials. Owing to their high strength-to-mass ratio, their relatively inert behavior in aggressive environments, their high hardness and wear resistance, and their ability to withstand significantly higher temperatures than metals or polymers, ceramics offer the potential for major improvements in component design for a wide range of applications. On the debit side, however, ceramic materials typically exhibit statistically variable brittle fracture, environmentally enhanced subcritical crack growth, sensitivity to machining damage, and creep/deformation behavior at elevated temperatures. Additionally, a lack of techniques, which can detect and quantify critical flaws before failure ensues, severely curtails current uses of ceramics. Unpredictable failure behavior of ceramics stems from three sources: (1) limited data and a deficiency of basic understanding of failure processes in ceramics; (2) limited standard test techniques to permit interlaboratory comparisons of materials behavior and collection of engineering data; and (3) inadequate models and statistical techniques for life prediction and reliability analyses. The Mechanical Properties of Brittle Materials Program has components specifically addressing each of these issues.

Basic understanding of mechanical behavior of ceramics is investigated at both room temperature and elevated temperatures. At room temperature, mechanical properties and failure processes are investigated in fiber-reinforced ceramic matrix composites as a function of microstructural scale and in aluminum nitride substrates as a function of processing conditions, phase content, and microstructure. Microstructural stresses related to enhanced fracture toughness are measured via micro-Raman techniques in heterogeneous microstructures and correlated with micro-mechanical modeling. Micro-mechanical computer simulations are used to elucidate distributions of residual stress distributions in highly anisotropic ceramics as a function of crystallographic texture. At elevated temperatures, the basic mechanisms responsible for crack growth, creep and creep rupture are investigated for various silicon nitride compositions, and for membrane and fuel cell materials.

To improve interlaboratory comparisons and to increase confidence in generated data, new standard test techniques for hardness and toughness are being developed and tested in round-robin experiments. Research and interlaboratory studies in instrumented indentation address the use of this technique for measuring elasticity and hardness of thin films and coatings. Micro-Raman techniques are being developed and calibrated so that quantitative assessments of microstructural residual stresses can be mapped for heterogeneous microstructures. At elevated temperatures, new creep specimens were designed which permit higher stresses with reduced non-gage section failures. Intra- and inter-laboratory studies demonstrated the robustness of these geometries. International interlaboratory studies are underway to elucidate their relationship to alternate testing geometries.

Finally, techniques to predict lifetimes of ceramics under constant and variable loading conditions are being developed. A nonparametric bootstrap approach for assessing the confidence of lifetime predictions is investigated and compared with analytical techniques. Work includes applying these techniques to aluminum nitride materials for thermal management systems and to fused silica and other glasses for spacecraft window applications. A new experimental procedure was developed for characterizing time-dependent failure under static loads.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Damage in Sapphire

Principal Investigators: David Black, Robert Polvani (Precision Engineering Division, MEL), Linda Braun, Grady White

Technical Objectives:

The combination of good optical and thermal properties makes large single crystal sapphire an ideal material for uncooled windows and domes for antiballistic missiles. In these applications the crystals experience large thermally induced stresses, which can lead to failure. One factor affecting the fracture strength of brittle materials is the presence of surface flaws. To produce windows and domes at the lowest cost with the highest reliability, processing induced surface and subsurface damage must be identified and minimized. Therefore, the technical objectives of this project are: 1) to develop diagnostic tools to detect surface and subsurface damage in sapphire; 2) to apply these techniques to characterize damage caused by growth and/or fabrication; 3) to correlate the observed damage to measured fracture strength; and 4) to evaluate the influence that post-fabrication processing procedures, such as annealing, have on surface and subsurface damage.

Technical Description:

The technical objectives of this project are being met with a series of experiments on sapphire modulus of rupture (MOR) bars. The bars are part of the Sapphire Statistical Characterization and Risk Reduction (SSCARR) program. This is an inter-service (Air Force, Army, and Navy) program designed to meet two needs: development of an engineering database for design engineers and exploration of new methods to improve the bulk strength of sapphire. The database combines the effects of crystal growth method, sample fabrication techniques, crystallographic orientation, and post-fabrication processing and represents all combinations currently used in antiballistic missile programs. Several methods are being considered to improve the strength of sapphire, such as thermal treatments, doping and surface coatings. Samples have been examined using the following techniques: light microscopy, polariscope, polarimetry, wavefront analysis, surface finish, polarized light ellipsometry, x-ray topography, Raman spectroscopy, neutron diffraction, and dimpling. Observations made by different techniques on the same samples allow us to select the best combination of diagnostic tools. Comparisons between observations made by the best techniques on different samples also allow us to investigate the relationship between growth and processing on surface and subsurface damage, as well as the effects of the post-fabrication processing procedures. An additional set of 90 MOR bars is being used to correlate defects observed by x-ray topography to the measured fracture strength.

External Collaborations:

Peter Lagerloff of Case Western Reserve University is involved in the preparation of samples and in the interpretation of data. Fred Schmid, Maynard Smith and Mark Felt of Crystal Systems Inc. grow high quality sapphire, supply samples with specific surface preparation and perform thermal

treatments. Dan Harris of the Naval Air Warfare Center supplies samples and helps in the interpretation of data. Fracture data are supplied by the University of Dayton Research Institute.

Accomplishments:

Characteristic microstructures for different growth methods have been identified using a variety of diagnostic tools. X-ray topography has been shown to be more sensitive to fabrication induced surface damage than optical techniques. We have observed that a "typical" high-temperature anneal affects the microstructure in the region that is ~100 nm below the surface, but not the long-range strain and subgrain structure. It was found that the application of a surface coating does not change the long-range strain field. A "zero stress/zero damage" reference sample has been selected and is in use as a standard for Raman spectroscopy and for emissivity measurements. A general expression that relates Raman peak shifts to stress has been derived for sapphire and some of the deformation potentials have been determined.

Publications:

D. Black, R. Polvani, L. Braun, B. Hockey and G. White, "Detecting Subsurface Damage: Studies in Sapphire," in Window and Dome Technologies and Materials V, Randall W. Tustison, Editor, Proceedings of SPIE Vol. **3060**, pp. 102-114 (1997).

D. Harris, F. Schmid and D. Black, "Factors that Influence Mechanical Failure of Sapphire at Elevated Temperature," in Window and Dome Technologies and Materials V, Randall W. Tustison, Editor, Proceedings of SPIE Vol. **3060**, pp. 226-235 (1997).

D. Black, L. Braun, H. Burdette, C. Evans, B. Hockey, R. Polvani and G. White, "Using Advanced Diagnostics to Detect Subsurface Damage in Sapphire," SPIE Conference: Optical Manufacturing and Testing II, San Diego Convention Center, San Diego, Ca, July 27-August 1, 1997.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Design of Space Shuttle Windows

Principal Investigators: Linda M. Braun, Jay S. Wallace, and Edwin R. Fuller, Jr.

Technical Objectives:

The objective of this project is to assist NASA through the development of measurement and analytical procedures, using a fracture mechanics based methodology, for determining mechanical reliability and for calculating projected lifetime of space application materials.

Technical Description:

This project involves measurement of mechanical properties, and development of analytical techniques that are required to determine mechanical reliability and to calculate the projected lifetime of brittle materials. Two different types of glass specimens are being investigated. The first is a fused silica used for space shuttle windows, and the second is a sodium aluminosilicate glass with and without a chemical temper used for space hatches. The thin, chemically tempered, layer is used to strengthen the glass.

The mechanical properties that are being measured include, fracture toughness, using double cantilever beam (DCB) and single edge pre-crack beam (SEPB) specimens, subcritical crack growth parameters, using DCB specimens, static fatigue, and dynamic fatigue tests, and *in situ* observations of crack propagation to failure. *In situ* measurements of crack size as a function of applied stress will be performed to determine the extent of crack propagation into the compressive tempered layer prior to catastrophic failure. Studies will include simulated proof test cycles and static load conditions to induce time-dependent delayed failure. This work will elucidate and quantify the stabilizing influence of the compressive tempered layer on the growth of cracks in the combined residual and flexural stress fields, thereby allowing realistic fracture mechanics analysis of crack stability and accurate prediction of reliability and lifetime.

External Collaborations:

This research is being conducted in collaboration with NASA, Boeing, and Corning, Inc.

Planned Outcomes:

The results from these experiments will be used to qualify (certify) both the fused silica and aluminosilicate glass for space applications. A comparison of the crack growth behavior of two grades of fused silica manufactured by Corning, Inc. will be performed.

Accomplishments:

We have designed experiments to measure the subcritical crack growth, fracture toughness, and dynamic fatigue behaviors of sodium aluminosilicate base glass. The equipment necessary to perform the experiments has been assembled.

We have designed experiments to measure the subcritical crack growth, fracture toughness, and static fatigue behaviors of fused silica. Static fatigue rigs have been designed and built. A new methodology for determining static fatigue is being developed.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: High Temperature Creep and Reliability

Principal Investigators: William E. Luecke and Sheldon M. Wiederhorn (MSEL)

Technical Objectives:

This research is designed to assist industry in the evaluation, design, and development of advanced structural ceramics for use as high temperature components in land based heat engines for power generation and vehicles, and in the development of measurement methodologies for the evaluation of the necessary high temperature mechanical properties.

Technical Description:

We are studying the mechanisms and statistics of high-temperature creep and rupture in advanced ceramics, and are developing and refining test methodologies for these measurements. Using our extensive creep facilities (9 tensile, 3 compression, and 6 flexure machines) we can generate the quantity of data necessary to make databases that allow statistical interpretation of the data. In addition, we can accommodate visiting scientists from industry and academia both to educate them on the use of our techniques as well as conduct tests on experimental grades of structural materials.

External Collaborations:

- Quian Jin and Prof. David S. Wilkinson, McMaster University, studying effects of tensile deformation on the amorphous grain-boundary film thickness in sintered silicon nitride.
- Dr. Wolfgang Braue, German Aerospace Research Establishment, Germany, examining microstructures of deformed silicon nitride samples.
- Daniel Grimme and Prof. Georg Grathwohl, Technical University of Bremen, Germany, characterizing effects of axial misalignment on tensile creep properties of silicon nitride.
- Robert Jensen and Prof. Nitin Padture, University of Connecticut, characterizing creep and failure of *in-situ* toughened silicon carbide.
- Siegfried Skirl and Prof. Jürgen Rödel, Technical University of Darmstadt, Germany, investigating creep of NiAl-Al_2O_3 metal-ceramic composites.
- Andreas Rendtel, Technical University of Hamburg-Harburg, Germany.
- International round robin for creep of silicon nitride between sixteen laboratories, including four in Japan and two in Europe.

Planned Outcomes:

Major outcomes of this research are expected to include: (1) Development of failure mechanism maps for structural ceramics proposed for use as ceramic engine components, including estimations of regions of low probability of failure; (2) Development of standardized tensile testing methodologies for material comparison; and (3) Elucidation of relationships between the microstructure of these materials and resultant elevated-temperature mechanical properties.

Additionally, the international creep round robin will make it possible to add a precision and bias statement to the ASTM standard for creep testing of ceramics, when it is revised next year.

Accomplishments:

The recent model for creep of silicon nitride has been refined so that it now has greater predictive capabilities. Its primary advantage, however, is that it is based on a specific microstructural model, unlike nearly all other models for creep of silicon nitride.

A second round robin for creep testing was initiated with support from the Electric Power Research Institute. This round robin, an international collaboration, involves sixteen laboratories, including four in Japan and two in Europe. They have received specimens and will begin testing soon.

In cooperation with Quian Jin and Prof. David S. Wilkinson of McMaster University the effects of tensile deformation on the thickness of amorphous grain boundary films, which are found in all sintered silicon nitrides were studied. This research will have important implications on possible models for primary creep of silicon nitride.

A collaboration with Dr. Wolfgang Braue of the German Aerospace Research Establishment was iniated to examine microstructures of deformed silicon nitride, which were tested in our laboratory. It has become clear that understanding the nature of second phase distributions is central to developing accurate models for tensile creep and structural reliability of silicon nitride.

In collaboration with Prof. Nitin Padture of the University of Connecticut the creep and failure behavior of *in situ* toughened silicon carbide was characterized. Robert Jensen, a masters degree student, spent six months working in our laboratory on this project.

In collaboration with Prof Jürgen Rödel of the Technical University of Darmstadt, Germany, the creep behavior of metal-ceramic composites was investigated. His graduate student, Siegfried Skirl spent three months at NIST conducting creep tests on a NiAl-Al_2O_3 material.

Publications:

Ralph F. Krause, Jr, William E. Luecke, and Sheldon M. Wiederhorn, "Comparison of Tensile Creep Measurements on a Hot Isostatically Pressed Silicon Nitride," J. Am Ceram. Soc. (1997), in review.

William E. Luecke and Sheldon M. Wiederhorn, "Interlaboratory Verification of Silicon Nitride Tensile Creep Properties," J. Am Ceram. Soc., **80**[4] 831-838 (1997).

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Mechanical Property Modeling

Principal Investigators: W. Craig Carter, Stephen A. Langer [Mathematical and Computational Sciences Division, ITL], Andrew R. Roosen, and Edwin R. Fuller, Jr.

Technical Objectives:

This research is designed to assist industry through the development of new paradigms for elucidating micro-physical behavior of real and simulated material microstructures. Theoretical and computational methods are applied to bitmap images to investigate microstructural stresses and strains, and fracture, deformation and damage behavior, and other nonlinear phenomena in polycrystalline and multi-phase ceramics and ceramic composites. A particular objective is the prediction and computation of behaviors in complex, real microstructures with the aim of identification of microstructural features which optimize macroscopic properties in real, commercial materials. Another technical objective is the dissemination of research expertise in the form of open, public-domain, software, which can be utilized by industrial materials scientists and other researchers to perform virtual materials testing.

Technical Description:

Microstructures in real materials are complex configuration which can contain distributed second phases, each having its their own localized constitutive behavior. Microstructures can also contain cracks, pores, and other features which severely affect performance. A general software tool, called ***OOF*** for **O**bject **O**riented **F**inite Elements, is being developed which incorporates all such complexity and which organizes local constitutive behavior so that calculations can be performed in systems which would otherwise be intractable. The research models the mechanics and physics of heterogeneous microstructures at the mesoscopic level.

External Collaborations:

This research involves numerous external collaborations. Informal joint projects include:

- Michael H. Zimmerman and Prof. Katherine T. Faber, Northwestern University
- Tom Isabell and Prof. Vinayak P. Dravid, Northwestern University
- Jill Glass, Sandia National Laboratory
- André Zimmermann and Prof. Jürgen Rödel, Technische Hochschule Darmstadt
- Prof. Wolfgang Pompe, Technische University Dresden
- Prof. Anil Saigal, Tufts University
- Chun-Hway Hsueh and Paul Becher, Oak Ridge National Laboratory

Additionally, more than one hundreds researchers have downloaded the ***OOF*** software from the CTCMS (Center for Theoretical and Computational Materials Science) Software archives, are using it, and are providing us feedback.

Planned Outcomes:

The ***OOF*** software, a new paradigm for computation on real microstructures, will be provided to the public in various stages of its development as its capabilities are extended to aid in the development and prediction of the performance of commercial materials through virtual materials testing.

Accomplishments:

A general, powerful, software tool, called ***OOF*** for **O**bject **O**riented **F**inite Elements, was produced, which allows a researcher to use a simple point-and-click interface to perform tests on complex microstructures. ***OOF*** is an interface to perform several tasks:

- Combine microstructural image data with materials data and constitutive behavior.
- Apply (virtual) experimental boundary conditions and/or stress-free localized strains.
- Solve for thermoelastic stresses and strain fields.
- Predict and incorporate materials damage.
- Quantify and visualize results.

OOF is based on a method of using image data from real or simulated materials to create a finite element mesh. The program includes image selection and manipulation, a finite element mesher and solver, and an extensive interface.

A description of ***OOF***, links to a beta version of the program which may be downloaded as public domain software, an interactive manual, and a "Picture and Simulation Gallery" are available on the Internet at URL address:

http://www.ctcms.nist.gov/~wcraig/oof/

Thus far, more than 100 copies of the program have been downloaded.

Specific accomplishments include:

- Evaluation and virtual testing performed on real and computed microstructures.
- Software was made publicly available in executable form.
- Web-based documentation of software made available.
- Microstructural data file formats were developed.
- Software was ported to widely available windowing system.
- Web-based documentation of subsidiary software (***PPM2OOF***) initiated.
- Wider range of material constitutive behaviors incorporated.
- New meshing schemes initiated.
- New visualization and post-calculation analysis tools developed.

Publications:

An on-line ***OOF*** Manual, URL address:

http://www.ctcms.nist.gov/~wcraig/oof/manual/manual.html

Anil Saigal, E. R. Fuller, Jr., A. A. Langer, W. C. Carter, M. H. Zimmerman, and K. T. Faber, "Effect of Interface Properties on Microcracking of Iron Titanate," *Scripta Met.*, submitted.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Mechanical Test Development

Principal Investigator: George D. Quinn

Technical Objectives:

Procedures are developed for characterizing ceramics, and standard test methods are prepared for ASTM and ISO consideration. Our goal is to develop procedures that are as technically rigorous as possible, while ensuring that they are practical and usable by industry.

Technical Description:

Mechanical testing methods for ceramics are created, developed, improved, refined, and standardized. Testing is conducted to gain first-hand experience with a method. Upon reaching a mature prestandardization level, a method is evaluated by round robin(s), which verify the suitability of the method and generate precision and bias data. Foundation work for standard reference materials is performed. Current work is targeted towards fracture toughness, hardness, and diametral compression strength tests.

External Collaborations:

Industry is consulted for test method standardization needs. The Department of Energy, Office of Heavy Vehicle Technologies, provides programmatic support for some portions of this project. ASTM Committees such as C-28, *Advanced Ceramics*, and F-04, *Surgical and Medical Devices* are consulted and used as forums for creating standards. International collaborations are maintained through the VAMAS program and other avenues as warranted. International standardization is pursued through ISO Technical Committee 206, *Fine Ceramics* and contacts in CEN Technical Committee TC 184, *Advanced Technical Ceramics.*

Planned Outcomes:

Standard test methods for advanced ceramics will be developed for fracture toughness, flexural strength, diametral compression strength, and hardness measurements.

Accomplishments:

In the last year, one new standard was shepherded through ASTM and adopted as a provisional standard based on the work done in this project: ASTM PS 070-97 *"Standard Test Method for the Determination of Fracture Toughness of Advanced Ceramics,"* (in collaboration with I. Bar-on, M. Jenkins, and J. Salem).

In addition, substantial progress was made in refinements to the Surface Crack in Flexure method, which is one of the three adopted in PS-070. Preliminary findings relative to on a candidate fracture

toughness Standard Reference Material have been quite positive. Work to exploit this positive outcome will accelerate in FY 1998.

Revisions to standard C 1211-92 *"Standard Test Method for Flexural Strength of Advanced Ceramics at Elevated Temperature,"* were also prepared and balloted in late 1997. Also, a new draft world standard was prepared for ISO TC 206: ISO - DIS draft international standard 14704 *"Test Method for Flexural Strength of Monolithic Ceramics at Room Temperature."*

Diametral compression strength testing has also begun, with a goal of eventual standardization. This method is suitable for small round specimens and may be a useful adjunct to flexure or tension testing.

We participated in four Versailles Advanced Materials and Standards (VAMAS) round robins in the past year:

1. Hardness of Ceramic Composites, organized by NIRIN - Sakaguchi / JFCC - Mizuno in Japan. NIST joined as a participating laboratory and G. Quinn helped to analyze statistically the results.

2. Recording (Instrumented) Hardness, organized by BAM - Ullner, Germany and by NIST - Quinn. This project featured a borosilicate crown glass and the NIST SRM 2830 Knoop Hardness standard. G. Quinn at NIST co-organized this round robin and D. Smith performed the NIST experiments.

3. Quantitative Microscopy II, organized by NPL - Morrell, England and CTK - Dortmans, the Netherlands. This project investigated volume fraction second phase, porosity, and manual versus automatic image analysis. Ms. H. Moupas and G. Quinn at NIST participated.

4. Fracture Toughness V, organized by EMPA - Kübler, Switzerland. This project featured an innovative simple method to precrack specimens with a razor blade and diamond paste. G. Quinn and K. Xu of NIST participated.

Refined and standardized test methods are now available. The ceramics community now has procedures that generate data of high quality and data which is readily comparable between laboratories, benefitting both the industrial and research communities. Data suitable for design and design data bases are now easily obtained. *The structural ceramics community now takes ceramics more seriously and are more inclined to utilize this class of materials.* Tangible benefits also include significant cost savings. For example, the adoption of standard specimen sizes and surface preparation treatments has driven the cost of flexure specimens (the bread-and-butter strength test for ceramics) from $15-20 per specimen to $8 per specimen, a 50% savings.

A specific example of the benefits of standardization is the draft standard, *"Standard Specification for Zirconia for Surgical Implants,"* from the new ASTM Committee F-04, *Surgical and Medical Devices*. This material specification standard, which will be used by the US Food and Drug Administration and ceramic manufactures in the United States, Germany, England, and France,

features *five standard that were prepared in this NIST program.* Zirconia will have to meet specified property levels for elastic modulus, hardness, and flexure strength.

As another example, fractography of ceramics has heretofore been a highly interpretive "art." Work in this project has standardized some elements of fractographic analysis. Consistent results and interpretations are more readily obtained and can be related better to mechanical property results. The fractography standard is used as a teaching aid in courses at several universities and by a course offered by The American Ceramic Society.

A new approach was devised for characterizing the brittleness of advanced ceramic materials. The technique, an "Indentation Brittleness Measure" is an outgrowth of the hardness SRM and standards research, which resulted in our ability for more precise indentation hardness measurements.

Publications:

J. B. Quinn and G. D. Quinn, "Indentation Brittleness of Ceramics: A Fresh Approach," J. Mat. Sci., Vol. **32**, 4331-4346 (1997).

G. D. Quinn, "ASTM Committee C-28 Advanced Ceramics: The First Ten Years," Am. Ceram. Soc. Bull., Vol. **75**, No. 12, 45-46 (1996).

J. J. Swab and G. D. Quinn, "Investigation of `Halos' Associated with fracture Toughness Precracks," Ceram. Eng. and Sci. Proc., **18** [4], 173-182 (1997).

G. D. Quinn, J. J. Swab, and M. D. Hill, "Fracture Toughness by the Surface Crack in Flexure (SCF) Method: New Test Results," Ceram. Eng. and Sci. Proc., **18** [4], 163-172 (1997).

J. B. Quinn and G. D. Quinn, "On the Hardness and Brittleness of Ceramics," Key Engineering Materials, Vol. **132 - 136**, Part 3, Proceedings of the European Ceramic Society Conference, June 1997, edited by J. Baxter, L. Cot, R. Fordham, V. Gabis, Y. Hellot, M. Lefebvre, H. Le Dousall, A. Le Sech, R. Naslain, and A. Sevagen, pp. 460 - 463.

G. D. Quinn, M. Jenkins, I. Bar-On, and J. Salem, "The New ASTM Fracture Toughness of Advanced Ceramics Standard," Key Engineering Materials, Vol. **132 - 136**, Part 3, Proceedings of the European Ceramic Society Conference, June 1997, edited by J. Baxter, L. Cot, R. Fordham, V. Gabis, Y. Hellot, M. Lefebvre, H. Le Dousall, A. Le Sech, R. Naslain, and A. Sevagen, pp. 2115-2888.

J. J. Swab and G. D. Quinn, "Effect of Precrack "Halos" on K_{Ic} Determined by the Surface Crack in Flexure Method," J. Am. Ceram. Soc., in press.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Residual Stress Measurements

Principal Investigators: Linda M. Braun and Grady S. White

Technical Objectives:

The objective of this project is to develop measurement procedures, using micro-Raman spectroscopy, to determine quantitatively grain-localized residual stresses which can influence the mechanical, electrical, and optical properties of materials.

Technical Description:

Raman spectra are generated by the interaction of light with phonon modes in the unit cell. Consequently, stress induced changes in unit cell symmetry will cause shifts in Raman peak position and intensity. We have used an *in situ* micro-Raman technique, with a lateral resolution of ~6 μm, to probe stresses/strains. Stress is correlated with shifts in the Raman peak position as a function of a known externally applied load; changes in stress as small as 10 MPa can be detected. The phonon deformation potential terms must be determined in order to relate quantitatively stress to peak shift. A major emphasis of this work involves investigating crystallographic effects on calibration curves. Peak shift/stress relationships were determined for [0001], [11$\bar{2}$0], and [22$\bar{4}$3] crystallographic orientations in sapphire using an *in situ* biaxial stressing rig. Effects of incident light polarization were also investigated in order to relate crystallographic orientation to Raman spectra. In the polarization studies, incident polarization angle was changed relative to the known crystallographic orientation. Crystallographic orientation was determined using electron backscatter techniques.

External Collaborations:

Modeling of the effect of stress on Raman spectra is being investigated in collaboration with Dr. Michael I. Bell of the Naval Research Laboratory (NRL). Stresses in sapphire windows are being investigated with Robert Polvani of the Precision Engineering Division, MEL, NIST. The effect of stress in duplex microstructures is being studied with A. J. Kamal and M. P. Harmer of Lehigh University. Stress effects on the reliability of thermal barrier coatings are being examined with M. Ferber at Oak Ridge National Laboratory (ORNL).

Planned Outcomes:

This work has demonstrated that specimen crystallographic orientation and polarization must be known for Raman peak positions to be related to stress state. An anticipated outcome of this work is the development of standardized calibration procedures for a quantitative stress determination for materials, which exhibit sharp Raman peaks and for which calibration of the peak shifts can be obtained.

Accomplishments:

We have demonstrated crystallographic orientation sensitivity of biaxial stress-peak shift calibration curves in sapphire. Three crystal orientations have been investigated as a function of applied biaxial stress. Variations in crystallographic orientation relative to the incident and scattered radiation have been chosen to provide independent equations which allow evaluation of the material constants relating stress to peak shift (i.e., phonon deformation potential terms). We have used the experimental results, from the three different crystal orientations in sapphire, to calculate the phonon deformation potentials for the non-degenerate peaks in sapphire.

Polarization effects have been measured for both Raman peak intensities and stress-dependent peak position. We have shown that the in-plane crystallographic orientation of the $(11\bar{2}0)$ sapphire specimens can be determined relative to an arbitrary laboratory reference frame by evaluating the relative Raman peak heights.

Residual stress induced peak shifts were measured in sapphire optics for the Ballistic Missile Defense Program (THAAD Windows and SCARR bars) (see Damage in Sapphire). Raman peak shifts were correlated with results from both polarized light microscopy and x-ray topography. We have investigated the effect of a high temperature anneal on the residual stress in sapphire optics (SCARR bars). The Raman results show little if any change in the residual stress state of the bar with annealing, in agreement with the results from both polarized light microscopy and x-ray topography.

Publications:

G. S. White and L. M. Braun, "Effect of Crystal Orientation and Polarization on Raman Stress Measurements in Sapphire," submitted to WERB.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Test Development for Electronic Substrates

Principal Investigators: Jay S. Wallace and Edwin R. Fuller, Jr.

Technical Objectives:

The primary objective of this research is to develop standard test methods for measuring the strength of aluminum nitride (AlN) and other thin substrate materials used in electronic packaging. A principle requirement for a test technique is that it be able to be used on materials in the as-fabricated condition, *i.e.,* without further sample preparation or grinding. Secondary objectives are to characterize the mechanical properties of commercial and prototype low-fired AlN materials, and to ascertain the microstructural factors which control the measured properties.

Technical Description:

Development of high-reliability substrate materials requires the characterization of mechanical behavior for materials which are fabricated with new powders and compositions. Unfortunately, standardized techniques for evaluating strength, three- and four-point bending of 3 mm to 4 mm thick bar samples, are incompatible with the geometry of the 0.5 mm to 1 mm thick tape-cast plates used as substrates. In order to meet the thickness requirements for conventional strength testing, the sample fabrication conditions would have to be extensively modified, raising questions whether the materials being tested are representative of production substrate materials. Furthermore, machining required by standard test protocols can either introduce new flaw populations into the material or remove existing flaw populations, resulting in test data that do not represent the behavior of the in-service material. The ring-on-ring technique being considered in this project could be used for testing electronic substrate materials in their in-service condition without further sample preparation.

External Collaborations:

This research is part of the *Japan-U.S. Research Collaboration in Aluminum Nitride* for pre-competitive research in the development of AlN materials. It is a four-way collaboration between Dow Chemical Company of Midland, Michigan, who provides AlN powder to Toshiba's Research and Development Center in Japan to make test specimens. NIST develops and conducts tests for characterizing the mechanical behavior of AlN substrates, and Japan's National Industrial Research Laboratory of Nagoya (NIRIN) is responsible for processing studies and microstructural characterization.

Planned Outcome:

The major outcomes expected from this research are: (1) development of testing methodologies for evaluating structural properties and reliability of thin ceramic substrate materials in their in-service condition and (2) an understanding and characterization of the microstructural factors that control the properties in these materials.

Accomplishments:

Since the ring-on-ring fixtures were designed and fabricated, the four participants in the program have participated in three AlN strength round robin tests. Results from the first round robin identified some difficulties in the design and fabrication of the testing fixture. The fixture problem, which was identified, was confirmed with finite element calculations. The second round robin identified interactions between the fixtures and the sample which lead to laboratory to laboratory irreproducability. The final round robin again raised concerns about the test fixture and sample to fixture interactions. These sample-to-fixture interactions were experimentally confirmed using strain gauged samples. Further strength testing and measurement of strain gauged samples with compliant layers between the fixture and sample have shown improved laboratory-to-laboratory consistency.

Microstructural evaluation has shown that the second phase distribution and composition in these materials can vary greatly, depending on the starting powders and processing conditions. However, their effects on strength are insignificant, unless there is a pronounced cracking tendency in the second phase. A near-surface layer, which would have been removed by grinding in conventional testing, was shown to have a strong influence on the strength of as-fired samples.

To date, five meetings have been held between the participants to exchange data. An International Conference on Aluminum Nitride is being organized for March 9-11, 1998 in Tokyo, Japan.

Publications:

J. S. Wallace, E. R. Fuller, Jr., and S. W. Freiman,"Mechanical Properties of Aluminum Nitride Substrates," NISTIT 5903, National Institute of Standards and Technology, Gaithersburg, MD (December 1996).

J. S. Wallace, E. R. Fuller, Jr, and S. W. Freiman, "Mechanical Properties of Aluminum Nitride Substrates," in Development of High Performance Aluminum Nitride Ceramics Through a Low Cost Process, Report Number 1, Japan-U.S. Joint Research Group on AlN Ceramics, New energy and Industrial Technology Development Organization (NEDO), February 1997), pp. 47-89.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Test Development for Membrane Materials

Principal Investigators: Edwin R. Fuller, Jr., Ralph F. Krause, Jr., and Tze-jer Chuang

Technical Objectives:

This research is designed to assist industry through the development of measurement techniques for the structural characterization of dual purpose oxygen conducting ceramic materials. Additionally, critical mechanical property data are collected for newly developed materials to facilitate design and fabrication of a ceramic membrane reactor for processing gas streams. Techniques for determination of mechanical properties and residual stress and methodologies for assurance of durability and reliability under specific service conditions are the primary NIST focuses. Mechanical properties include: Young's modulus, strength distribution, residual stress evaluations, subcritical crack growth behavior for life predictions, and fracture toughness.

Technical Description:

Testing methods are evaluated, improved, and refined for measuring mechanical properties of small, brittle tubular specimens at elevated temperatures and in controlled environments. Key mechanical properties affecting design include: strength, residual stress state, and elastic modulus. Those properties affecting lifetime and reliability include: Weibull properties, residual stress state, subcritical crack growth behavior, and fracture toughness. Special considerations are needed due to the interplay between component geometry, compositionally driven residual stresses, and environmental history. Efforts have focused on an O-ring testing configuration for characterizing strength and a C-ring configuration for evaluating Young's modulus. Existent candidate materials are evaluated to validate testing techniques and to provide preliminary data to facilitate design and fabrication of reactor components. Finite element and analytical analyses support the test method development. Coupled diffusional equations with misfit stress calculations aid in evaluating the influence of the compositionally driven residual stress state.

External Collaborations:

Terry J. Mazanec and Ajit Sane, BP Chemicals Inc., Cleveland, OH
G. Whichard and V. Bergsten, Praxair Surface Technologies, Indianapolis, IN

Planned Outcome:

The major outcomes expected from this research are: (1) development of testing methodologies to quantify structural properties and reliability of oxygen conducting ceramic membranes; (2) an understanding and characterization of failure and damage mechanisms in these materials, and (3) an understanding of compositionally driven residual stress states in these materials and their influence on structural behavior and lifetime.

Accomplishments:

Techniques were developed for testing small O-ring specimens in controlled gaseous environments from room temperature to 1000 °C. Mechanical strengths were measured on specimens cut directly from ceramic membrane tubes at room temperature in air and at 1000°C in nitrogen and in select oxygen-nitrogen mixtures. Weibull properties were evaluated. A theory was derived for the time-dependent residual stresses that result from diffusion induced misfit strains. The residual stress state of a membrane tube was evaluated for boundary conditions such that the tube is initially in an oxygen depletion state. An analysis, both analytical and via finite elements, of the gap displacement for a C-ring testing geometry illustrates that the C-ring testing configuration provides a viable technique for measuring Young's modulus at elevated temperatures, if the gap distance can be measured with an uncertainty of ~2 μm.

A meeting was held at NIST on June 2, 1997, and to have the results were delivered to an ATP awardee. Dr. Terry J. Mazanec from BP Chemicals Inc. Cleveland, OH attended the meeting as well as two persons from Praxair.

SYNCHROTRON RADIATION

SYNCHROTRON RADIATION CHARACTERIZATION

The availability of synchrotron radiation is resulting in major discoveries over a wide range of disciplines within materials science. The Synchrotron Radiation Program is a development and characterization effort which includes the operation of beam stations at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, construction of beam stations at the Advanced Photon Source in a Collaborative Access Team (CAT) arrangement with the University of Illinois, Oak Ridge National Laboratory, and U.O.P. Corporation, and a microstructural characterization effort in which NIST scientists, and researchers from industry, universities and other government laboratories perform state-of-the-art measurements on advanced materials.

The range of scientific problems currently being addressed at the NSLS includes: microstructure characterization of portland cement, ultra-high-molecular weight polyethylene, man-made diamonds and diamond films, sapphire windows, and GaN films on sapphire. Most recently, an *in situ* investigation of the formation of dislocation structures has been initiated successfully. *In situ* microstructure characterization, using ultra-small-angle scattering, x-ray imaging, and ultra-soft-x ray absorption spectroscopy is a very active area. Other areas of intensive investigation include studies of bond lengths in strained semiconductor layers, tribochemical reactions on surfaces, the orientation of lubricants on hard disk magnetic media substrates, order and orientation of proteins bound to self-assembled monolayers, and the development of new catalysts.

A wide range of materials studies were carried out at NSLS during 1997. The ultra-small-angle scattering facility (USAXS), which is used to examine microstructures from tens of angstroms up to micrometers in size, has yielded significant results, for example, on the microstructure of ultra-high-molecular-weight polyethylene, on portland cement and plasma-sprayed ceramics, on semi-crystalline polymers, on metal-binding by pseudomonas aeruginosa, on the structure of bovine bone, on additive dispersions in polycarbonate, and on the dislocation structure of single crystal aluminum under stress. The USAXS instrument fills the gap between visible light scattering and pinhole small-angle cameras. As one of the few SAXS instruments in the world for which a primary absolute calibration is available, the results from the X23A3 USAXS facility are typically quantitative rather than qualitative.

The high-resolution, monochromatic x-ray topography camera at the NSLS facility is the only dedicated monochromatic facility of its type in this country. In the past year, it was used in studies of a range of basic and applied materials including sapphire, superconducting YBCO crystals, CVD diamond, and single-crystal Al. The hard x-ray microscope, which was designed and built by NIST researchers, offers unique opportunities to perform *in situ* x-ray diffraction imaging and high-resolution x-ray radiography measurements.

Research by NIST scientists during 1997 included:

- studies of the relationship between microstructure development in hydrating cement and the morphology of additives,
- fundamental measurements of dislocation formation as a function of strain in single-crystal materials,
- studies of defects in superalloy single-crystal castings and sapphire windows,
- studies of the chemistry and the orientation of lubricants on hard-disk magnetic-media substrates,
- studies of tribochemical reactions in nanometer lubricant films,
- theory and experiment on bond-length distortions in strained-semiconductors.

PROGRAM TITLE: Synchrotron Radiation

PROJECT TITLE: Beamline Operation and Development

Principal Investigators: Gabrielle Long, Andrew Allen, David Black, Hal Burdette, Dan Fischer, Lyle Levine, Richard Spal, and Joseph Woicik

Technical Objectives:

The technical objectives of this project include the operation of two materials science x-ray beam stations (X23A2 and X23A3) at the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory for diffraction imaging, x-ray radiography, ultra-small angle x-ray scattering (USAXS), x-ray absorption fine structure (XAFS), and standing wave x-ray measurements. NIST is also a partner in the operation of two additional beam stations (U7A and X24A) for ultra-soft-x-ray absorption measurements and soft x-ray standing-wave measurements.

The other major technical objective is the development, construction/commissioning and operation of beam lines on Sectors 33 and 34 at the Advanced Photon Source (APS), at Argonne National Laboratory with NIST's Collaborative Access Team (CAT) partners—University of Illinois, Oak Ridge National Laboratory, and UOP Corporation—for high-resolution diffraction, USAXS, surface and interface scattering, XAFS, diffuse scattering, x-ray microbeam and coherent scattering.

Technical Description:

The Synchrotron Radiation Program involves the development and the operation of beam stations at the NSLS and the construction and operation of beam stations with our CAT partners at the APS. Currently, more than 100 scientists per year from NIST, and from industry, universities and other government laboratories, come to the NIST advanced materials characterization beamlines at the NSLS to perform state-of-the-art measurements. The USAXS instrument at the NSLS fills the gap between visible light scattering and pinhole small-angle cameras, and as one of the few SAXS instruments in the world for which a primary absolute calibration is available, the data from the NIST USAXS facility are quantitative rather than qualitative. The high-resolution, monochromatic x-ray topography camera is the only dedicated monochromatic facility of its type in this country, and is the only instrument able to support experiments at the highest resolution. A charge-compensation capability was recently installed on the soft-x-ray endstation, U7A, where the use of charge compensation enables reliable electron yield spectra to be obtained from macroscopically thick (mm) polymer samples. This opens the door to surface studies of industrially-important surface polymer treatments. Previous to this development, electron yield experiments on polymers were restricted to very thin layers (0.1 nm) or not possible at all.

The range of scientific problems currently being addressed at the NSLS includes: microstructure characterization of portland cement (see, "Characterization of Cements" under Other Programs), ultra-high molecular weight polyethylene, sintering of nanophase ceramic oxides, defects in man-made diamonds and diamond films, sapphire windows, and GaN films on sapphire. Most recently,

an *in situ* investigation of the formation of dislocation structures has been initiated successfully. *In situ* microstructure characterization, using ultra-small-angle scattering, x-ray imaging, and ultra-soft x-ray absorption spectroscopy is a very active area. Other areas of intensive investigation include studies of bond lengths in strained semiconductor layers, metal binding by pseudomonas aeruginosa, tribochemical reactions on surfaces, additive dispersions in polycarbonate, the orientation of lubricants on hard disk magnetic media substrates (see under "Magnetic Materials"), order and orientation of proteins bound to self-assembled monolayers, superconducting YBCO crystals and tapes (see under "High Temperature Superconductivity"), and the development of new catalysts.

Accomplishments:

In the area of instrument development for the APS, the components for the beam conditioning table for the high resolution x-ray diffraction hutch are currently undergoing testing prior to installation and commissioning at the Argonne facility. The newly constructed four-reflection USAXS, including the new silicon optics, has been characterized, and significant increase in resolution, decrease in background, and concurrent improvement in signal-to-noise, were observed. The new instrument operates at theoretical levels and will be available for shipment to the APS early in 1998.

The Final Design Report for the bending magnet beam line is now complete. All of the radiation enclosures have been ordered through APS with an anticipated construction date starting in early 1998. The mirrors and the double-crystal monochromator specifications are complete and bids are going out. The UNICAT staff are preparing specifications for all of the optical components to be ordered through vendors. The XAFS subgroup has selected design criteria and has set procurement priorities.

On the insertion device beamline, the double-crystal monochromator has been retrofitted by the vendor to increase the sliding range of the second crystal, thus permitting access to low energies, e.g. 4 keV. The modification is now complete and the system is undergoing testing. The second crystal bending device is being tested as well. Two commissioning experiments were carried out in the August-September run and more are anticipated in the January, 1998 running period. Starting FY98, sector 33-ID construction will be completed and commissioning and operations will be in full effect.

Funding for the coherent x-ray diffraction endstation for Sector 34 has been secured by the University of Illinois from the NSF, and DOE has made a commitment to fund the construction of the x-ray microprobe endstation. The rest of the construction funds will come from the State of Illinois and UIUC-MRL. Specifications for the sector 34 radiation enclosures are under development. A prototype Kirkpatrick-Baez mirror based x-ray microprobe will be put together by ORNL.

A number of significant findings arose from the research performed at NSLS:

Studies of the relationship between microstructure development in hydrating cement and the morphology of additives have been key to development of appropriate additives in this widely used material. Fundamental measurements of dislocation formation as a function of strain in single-crystal materials are leading to an improved understanding of the strength of metals and alloys. Studies of

defects in superalloy single crystal castings and sapphire windows have led to improved processing protocols. Studies of the chemistry and the orientation of lubricants on hard disk magnetic media substrates have indicated that the lubricant may have penetrated the overcoat, something which was not believed to happen, and now open the door to possible remediation. Research into the theory and measurement of bond length distortions in strained semiconductor alloys is leading to a unifying picture of macroscopic elasticity and the microscopic distortions which arise from alloying and pseudomorphic strain.

External Collaborators:

Haydn Chen and T. C. Chiang, University of Illinois, Gene Ice and Ben Larson, Oak ridge National Laboratory, Robert Broach, UOP Corporation, H. Boukari and M. Harris, University of Maryland, M. Goldman and L. Pruitt, U. of California/Berkeley, G. Beaucage and D. Schaefer, U. of Cincinnati, R. Livingston, Federal Highway Administration.

Planned Outcome:

The availability of synchrotron radiation is resulting in major discoveries over a wide range of topics in advanced materials science and processing. The APS offers a 100 to 10,000-fold increase in brilliance compared to the best synchrotron x-ray sources of today, and thus, in the years to come, the APS will supplant the NSLS as this nation's premier x-ray source. The new NIST facilities at the APS will extend our present portfolio of characterization capabilities to include and even wider range of advanced materials measurements of importance to materials scientists and U.S. industry.

Publications:

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Beaucage, G., J. H. Aubert, R. R. Lagasse, D. W. Schaefer, T. Reiker, P. Ehrlich, R. S. Stein, S. Kulkarni, and P. Whaley, "Nanostructured Semi-crystalline Polymer Foams," J. Polymer Sci. and Polymer Phys. **34** [17] (1996) pp. 3063 - 3072.

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Pehrsson, P., T. McCormick, B. Alexander, M. Marchywka, D. Black, J. Butler, and S. Prawler, "Homoepitaxial Mosaic Growth and Liftoff of Diamond Films," in Diamond for Electronic Applications, Proc. MRS Symp. Vol. **416**, Ed. D. L. Dreifus (1996) pp. 51 - 56.

Schaefer, R. J., D. R. Black, M. D. Vaudin, B. R. Mueller, A. F. Giamei, "Geometry and Mechanism of Dendrite Misalignment in Superalloy Single Crystal," Conference on Solidification Processing, Sheffield, UK, July 7-10, 1997.

Spal, R. D., "Theory of the Asymmetric Bragg Diffraction Microscope," to be submitted J. Appl. Phys. (1997).

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Semiconducting Materials Evaluation

Principal Investigators: Joseph C. Woicik, Bruce Steiner, and Lawrence Robins

Technical Objectives:

The technical objectives of this project are to characterize quantitatively the atomic scale structure of advanced semiconductor materials and to obtain a unified description of bond lengths, elasticity, and strain accommodation in semiconducting thin film structures.

Technical Description:

Advances in crystal growth techniques over the last two decades, such as the development of molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD), have enabled the synthesis of novel device structures from chemically dissimilar materials. These pseudomorphically grown heterostructures form the basis of semiconductor heterojunction device technology. A primary issue for both electronic and opto-electronic applications is the critical stress which must be accommodated across the interface due to the physical size mismatch of the constituent materials. When this stress is not accommodated elastically, the resulting defects in the films severely hamper electron transport and hence device performance. By utilizing intense, highly collimated synchrotron x-ray sources, we are able to perform high resolution extended x-ray adsorption fine structure, x-ray diffraction, and x-ray standing wave studies to determine quantitatively the atomic scale structure of these materials.

External Collaboration:

J.G. Pellegrino (EEEL, NIST) has grown the III-V materials by molecular beam epitaxy. C.A. King (Lucent Technologies, Bell Laboratories) has grown the IV-IV materials by CVD. D.K. Wickenden (Johns Hopkins) has provided AlGaN thin films grown by MOCVD. K.E. Miyano (Brooklyn College), L.B. Sorensen (University of Washington), and MJ. Bedzyk (Northwestern University) have participated in the measurements.

Planning Outcome:

A unified description of macroscopic elasticity and the microscopic distortions which arise from alloying and pseudomorphic strain will be developed.

Accomplishments:

Bond length strain in strained-layer semiconductors has been examined experimentally. The In-As and Ga-As bond lengths in strained InGaAs alloys were found to follow a simple model derived from macroscopic scale elastic theory and the virtual crystal approximation where the In-As and Ga-As bond lengths are distorted uniformly despite their inequivalent lengths. Additionally, the bond

lengths in AlGaN alloys were measured as a function of alloy composition and were found to remain close to their natural, bulk bond lengths. These finding demonstrate that the alloy accommodates the size mismatch of Al-N and Ga-N bonds primarily by means of energetically favored bond angle distortions rather than bond length distortions.

Publications:

J.C. Woicik, JG. Pellegrino, B. Steiner, K.E. Miyano, S.G. Bompadre, L.B. Sorensen, T.-L. Lee, and S. Khalid, "Bond-length distortions in strained-semiconductor alloys," to be published, Physical Review Letters.

J.C. Woicik, J.G. Pellegrino, and K.E. Miyano, "Bond lengths and elasticity in strained-layer semiconductors, "Journal De Physique IV**7**, 687 (1997).

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PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Studies of Irregularity in Optoelectronic Materials

Principal Investigator: Bruce Steiner

Technical Objectives:

The insight into crystal regularity that is the *scientific* objective of this activity provides an essential cornerstone for the design and effective commercial realization of novel single crystals for the next generation of photonic and electronic devices in the US. Current technical *targets* include advanced radiation detectors and guided wave modulators for enhanced position sensors and maximum capacity communications. These devices are being designed to increase simplicity and reliability in monitoring nuclear technology (for the DoE Safeguards Program, nonproliferation, storage of sensitive nuclear materials, portal monitoring, nuclear medicine, astrophysics), to augment sensitivity in orientation during travel, and to enable innovative approaches to information processing (for increased rapidity in computing and increased capacity in communications). Priorities are established and research carried out in collaboration with colleagues in industry, governmental laboratories and mission agencies, and universities.

Technical Description:

These technical objectives are achieved through the exploitation of NIST high sensitivity crystal characterization facilities and expertise in the crystalline irregularity that is associated with advanced crystals. The NIST Materials Science and Engineering Beamline at the National Synchrotron Light Source, X23A3, is used in conjunction with *in situ* laser optical fields. High resolution diffraction imaging, guided by the experimental and interpretive expertise established through this activity, leads to the identification of crystalline irregularity, the study of its influence on device performance, the determination of its genesis, and the achievement of its control through processing. The resulting insight provides a reliable basis for device design, performance optimization, and economical production of novel devices for the next generation of information processing technology

Activity currently includes: (1) lithium niobate crystals and guided wave modulators derived from them for fiber optic gyroscopes for increasingly precise position sensors, (2) mercuric iodide grown in microgravity and on the ground for optimized low-noise, room- temperature, high-energy radiation detectors, and (3) III-V layered systems for innovative high speed electronics

External Collaborations:

Collaboration in the development of high sensitivity fiberoptic gyroscopic devices and systems by Litton Guidance and Control Systems, for precise position sensing, has been supported by DARPA MANTECH in the Department of Defense. Collaboration with Crystal Technology, Inc., is supporting the production of x-cut lithium niobate crystals for this program. Collaboration with the Optoelectronics Division of the NIST Electronics and Electrical Engineering Laboratory (EEEL) supports the development of critical understanding of diffusion in these crystals, while collaboration

with the Semiconductor Electronics Division of EEEL supports the production and study of innovative III-V materials and devices. Collaboration with Constellation Technology, Inc. is supporting the continuing commercial development of mercuric iodide detectors for high energy radiation, following a Department of Energy program in nuclear sensors and NASA microgravity crystal growth programs.

Planned Outcome:

Four major results are planned: control over the yield in waveguide modulator fabrication for fiber optic gyroscopes for increased position sensitivity; determination of the evolution of strain during growth of lithium niobate crystals used in fiber optic position sensors and enhanced capacity in fiber optic communications; effective reduction in the removal of wafer material in cutting and polishing in order to achieve increased flatness for advanced photonics; and enhanced performance of low noise, room temperature, high energy radiation detectors based on knowledge gained from mercuric iodide crystals grown in microgravity.

Accomplishments:

Intermittent formation of processing induced layers in lithium niobate has been observed for the first time and shown to influence the formation and performance of associated waveguides. This interaction has been shown to be a principal source of uncontrolled variation in the yield of waveguide modulators. Progressive development of strain during growth of lithium niobate single crystals has been observed and shown to lead ultimately to subgrain structure, which affects the establishment of waveguides in these materials. The resulting modification in the crystal growth parameters for lithium niobate has been demonstrated to reduce effectively the development of strain during growth.

Fundamental insight has been achieved into the crystallographic origins of the enhanced performance of low noise, room temperature, high energy radiation detectors made from mercuric iodide.

Impacts:

Yield in fabrication of waveguide modulators for fiber optic gyroscopic position sensors is being brought under satisfactory control. Growers of highly uniform lithium niobate single crystals are now able to make economical trade-offs in crystal perfection and performance. Performance of room temperature, high energy radiation detectors made from mercuric iodide grown on the ground is now being optimized, approaching the superior performance of crystals grown in space.

Publications:

G. Fogarty, B Steiner, M. Cronin-Golomb, U. Laor, M. H. Garret, J Martin, and R. Uhrin, "Antiparallel ferroelectric domains in photorefractive barium titanate and strontium barium niobate observed by high-resolution x-ray diffraction imaging," J. Opt. Soc. Am. **B 13**, 2636-2643 (1996)

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Bruce Steiner, Mark Garret, Robert Uhrin, John Martin, Irina Mnushkina, William Burns, Norman Sanford, Alexana Roshko, Andrew Aust, Ka Kha Wong, and Gerard Fogarty, "Regularity in poled piezoelectric crystals," ONR Piezoelectric Crystal Planning Workshop, 16 May 1997

J. A. Aust, N. A. Sanford, A. Roshko, J. Amin, B. Steiner, C. Evans, G. Fogarty, and B. Yang, "Examination of domain-reversed layers in z-cut $LiNbO_3$ using maker fringe analysis, atomic force microscopy, and high resolution x-ray diffraction imaging," CLEO Tech. Digest 485 (1997)

Bruce Steiner, Lodewijk van den Berg, and Uri Laor, "Enhancement of Mercuric Iodide Detector Performance through growth in microgravity: the roles of lattice order," Prog. Mater. Res. Soc. **Symp. I3.5**, 68 (1997).

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Supported Catalysts

Principal Investigator: Daniel A. Fischer

Technical Objectives:

The objective of this project is to characterize the thermal chemistry of adsorbed propylene on Ag/TiO_2 using fluorescence-yield near-edge x-ray adsorption fine structure (NEXAFS) at the carbon K edge.

Technical Description:

As part of an ATP award "Breakthrough Process for the Direct Oxidation of Propylene to Propylene Oxide" the chemisortion of propylene on dispersed silver using fluorescence-yield NEXAFS at the carbon K edge was studied.

External Collaborators:

Jeffrey T. Ranney (U. of Michigan), Deborah H. Parker (The Dow Chemical Co.), Robert G. Bowman (The Dow Chemical Co.), George Hartwell (The Dow Chemical Co.), and John L. Gland (U. of Michigan).

Planned Outcomes:

The reaction intermediates that play an important role in catalytic partial oxidation will be determined. Such an identification of reaction intermediates is crucial to the development of a molecular understanding of catalytic reactions.

Accomplishments:

The room temperature chemisorption and nearly complete rehybridization of propylene on dispersed silver support on TiO_2 (anatase) has been observed for the first time. The intensity of the propylene C 1s to pi* resonance is nearly extinguished upon chemisorption of propylene on the catalyst at 300K. The loss of the pi* resonance indicates substantial rehybridization of the C-C double bond resulting in a reversibly adsorbed di-sigma bonded surface species. When adsorbed at liquid nitrogen temperatures, both the adsorbed and the condensed propylene retain their pi character. No propylene adsorption is seen on the neat TiO_2 support even at 115 K and propylene does not absorb on silver single crystals above 200 K. Therefore, we propose that the room temperature adsorbed propylene is related to areas of strong interaction such as the perimeter of the silver particles. This is the first direct observation of chemisorbed reactant monolayers on supported powders.

Publications:

"Direct observation of room temperature propylene adsorption and rehybridization on support silver using synchrotron radiation," J. Ranney, D. Fischer, D. Parker, G. Hartwell, J. Gland, submitted to Nature (1997).

THIN FILM MEASUREMENTS AND STANDARDS

THIN FILM MEASUREMENTS AND STANDARDS

Functional ceramics (*e.g.*, ceramics primarily intended for optical, electronic, or thermal management applications) are increasingly being used in film geometries. In response to this growing segment of the ceramics community, the Thin Film Measurements and Standards Program endeavors to provide improved measurement tools and data that are needed to evaluate advanced ceramic films and film systems. Increasingly critical film performance requirements (*e.g.*, reduced dimensions, increased purity, improved interface properties, increased production rates, and tighter control of properties) place stringent demands on film processing control, models, and characterization techniques. However, lack of measurement methods to monitor film processing and accurately characterize film properties as well as limited theoretical understanding of interrelationships between processing conditions and final film properties reduce most film processing to empirical procedures. The activities in this program are designed to address these measurement and modeling issues, both with regard to specific, near term industrial needs as well as to the development of a materials science knowledge base required for use of ceramic films in future applications. Near term and long range goals have been developed based upon both general discussions between Materials Science and Engineering Laboratory staff and representatives of industry and universities at professional meetings and consortia workshops as well as focused, collaborative research projects with specific organizations.

The film characterization techniques in use or under development include electrical, mechanical, optical, thermal, and x-ray measurements. Specific research activities include:

- investigations of the processing and microstructural features that control poling behavior and domain stability in ferroelectric films;

- development and utilization of spectroscopic procedures to evaluate film composition in $BaTiO_3$ and to detect defects in ferroelectric and semiconductor films;

- development of methods to measure and statistically analyze texture and texture distributions in films and to relate these data to processing conditions;

- development of measurement procedures, models, and standards to permit quantitative evaluation of thermal diffusivity in thin films and to relate thermal diffusivity to film microstructure and morphology;

- application of advanced x-ray measurement capabilities (*e.g.*, EXAFS, DAFS) to the analysis of film structure and composition and the construction of an in-house state-of-the-art x-ray facility.

A critical requirement for the projects cited above is the ability to generate model film systems. To this end, this program includes two film deposition capabilities: metalorganic chemical vapor deposition (MOCVD) and pulsed laser deposition (PLD). The MOCVD system is an integral part of the ferroelectric film research projects already listed and, during the past year, has undergone a major upgrade to provide more precise compositional control. In contrast, the PLD facilities, while

providing films for investigation, has had an additional responsibility - the development of *in situ* measurement procedures to monitor the physical and chemical processes involved during the film deposition process and the formation of models to relate the measurements to the film formation.

PROGRAM TITLE: Thin Film Measurements and Standards

PROJECT TITLE: Ferroelectric Poling and Domain Stability

Principal Investigators: John Blendell, Lawrence D. Rotter, and Debra L. Kaiser

Technical Objective:

The primary objective of this research is to develop measurement techniques for evaluating ferroelectric domain structure, poling efficiency, and domain stability that will assist U.S. industry in the commercialization of ferroelectric oxide thin films for electronic and optoelectronic applications. This research will also provide a fundamental understanding of the effect of residual stress and microstructural defects on the domain structure and stability in thin films.

Technical Description:

Ferroelectric materials are characterized by the presence of domains, which are regions of uniform electrical polarization that can be switched from one orientation to another by application of an electric field. The domain structure, or arrangement of domains with different polarization orientation, dominates the properties of ferroelectric oxide thin films and their performance and reliability in integrated ferroelectric nonvolatile memory devices, microelectromechanical systems (MEM's), pyroelectric detectors, and optoelectronic devices. For example, in the case of the memory devices, the individual domains or groups of domains that comprise a single memory cell must have negligible polarization fatigue, i.e., the domain orientations must not be a function of time, upon repeated read/erase/write operations. Similarly, polarization retention is important for optoelectronic applications where the optimal structure is a single domain. Regardless of the application, it is necessary to be able to determine the domain structure in the film and to assess the efficiency of switching the polarization and the stability of the polarization state. Since the structure, polarizability and stability of the domains are strongly influenced by residual stresses and defects such as impurity atoms or charged oxygen vacancies, knowledge of these microstructure/property relationships will aid in the industrial development of ferroelectric oxide thin film technologies.

Planned Outcome:

This research will provide present and future U.S. companies engaged in ferroelectric oxide thin film device development with appropriate measurement tools to evaluate domain structure, polarization efficiency and domain stability in ferroelectric thin films. In addition, the research will provide a fundamental knowledge base of the microstructure/property relationships relevant to these domain issues.

Accomplishments:

Most film systems are heterostructures composed of two or more layers of differing composition; a single film layer on a substrate is the simplest form of film heterostructure. The interactions between the different layers during film growth result in residual stresses that have a profound effect on the domain structure in the ferroelectric layers. A theoretical study of the thermodynamic principles governing the formation of polydomain heterostructures in ferroelectric and superconductor oxide layers was completed by guest researcher Alexander L. Roytburd, University of Maryland. Residual stresses in constrained layers composed of epitaxial films or multilayers can result in differently oriented domains of the same phase (twins) or domains of different phases. The conditions for the formation of polydomain heterostructures were established on the basis of the analysis of thermodynamic effects of internal and external macrostresses on phase transformations. Microstresses that arise due to the periodic deviation of the actual misfit from the average misfit on the interfaces between a polydomain layer and neighboring layers were also considered in the analysis. It was determined that polydomain heterostructures are always more stable than single domain structures. Also, there is a critical thickness for the polydomain structure below which the structure becomes unstable or changes symmetry.

Films can contain undesirable secondary phases that introduce additional residual stresses during cooling due to differences in the thermal expansion coefficients of the secondary phases and the ferroelectric material, thereby influencing the domain structure. We have initiated a theoretical study of the effect of secondary phases on the formation of domains in ferroelectric oxide thin films. The results of this study will be coupled to ongoing experimental studies of the effect of domain orientation on the fraction of amorphous second phases in thin films containing ferroelectric $BaTiO_3$ and amorphous material. It is difficult to detect the presence of amorphous material in films or to quantify the amorphous fraction by routine characterization methods such as conventional θ-2θ x-ray diffraction. Consequently, we have been developing methods based on glancing angle x-ray diffraction, EXAFS, Raman spectroscopy and optical transmission spectroscopy to quantify the fraction of amorphous material in films. More details on the optical and x-ray measurements are presented in the project reports on Optical Characterization Techniques and X-ray Characterization of Photonic Materials.

Atomic force microscopy has been used to image 90° domain boundaries in bulk $Pb(Zr,Ti)O_3$ samples that were polished and etched in phosphoric acid. The domains were 200 nm to 500 nm in width and the grain size in the samples was 3 μm to 4 μm. Repeated experiments have demonstrated that the polishing and etching procedures do not modify the domain structure in the material. Subsequent annealing above the Curie temperature has permitted a direct visualization of changes in the domain structure within individual grains before and after depoling. To our knowledge, this is the first observation of the effect of depoling within individual grains by atomic force microscopy. This technique is intended to be used to investigate thermal, electric field, and stress effects on domain stability in $PbTiO_3$ and $Pb(Zr,Ti)O_3$ thin films.

In preparation for electrical poling experiments, a photolithographic liftoff method was developed for depositing interdigitated metallic electrodes on the surfaces of thin films containing $BaTiO_3$ on insulating MgO substrates. The line width of the electrodes is 10 μm and the spacing between lines

is 10 μm. This research is also discussed in the project report on Optical Characterization Techniques.

Publications:

"Thermodynamics of Polydomain Heterostructures. I. Effect of Macrostresses," Alexander L. Roytburd, accepted in J. Appl. Phys.

"Thermodynamics of Polydomain Heterostructures. II. Effect of Microstresses," Alexander L. Roytburd, accepted in J. Appl. Phys.

PROGRAM TITLE: Thin Film Measurements and Standards

PROJECT TITLE: *In Situ* Process Monitoring and Control

Principal Investigators: John W. Hastie, David W. Bonnell, Albert J. Paul, and Peter Schenck

Technical Objective:

The project seeks to develop molecular level measurement capabilities needed (a) to monitor, *in situ* and in real time, the vapor deposition of thin films using pulsed laser deposition (PLD) and metal organic chemical vapor deposition (MOCVD) methods; and (b) to provide basic data for development of process models.

Technical Description:

Owing to the short time scale involved (nanosecond to microsecond for PLD) and the chemical complexity of the deposition species, several types of complementary measurement techniques are required to make real time process measurements. Development of new measurement and modeling approaches describing the vapor-substrate interaction and film growth are a focus of current investigation. The measurement methods and process models developed are intended to allow industry to utilize in-process monitoring for optimum control of the resultant thin film properties. These capabilities should reduce the need for time consuming empirical derivation of optimal processing conditions and extensive post processing analysis currently used in industry.

Measurement approaches developed earlier continue to be refined for this project, and they include, primarily: molecular beam sampling mass spectrometry (MBMS), optical emission and absorption spectroscopy (developed this year) coupled with optical multichannel analysis, and optical imaging utilizing high speed intensified charged-coupled device (ICCD) detection. The measurement methods are complemented by process model development based on coupled fundamental processes, including hydrodynamics, thermodynamics, and chemical kinetics. Using the combined real-time results of optical spectroscopy, optical imaging and molecular beam mass spectrometry, molecular-level models are being developed and tested for the PLD process. Related work is in the planning stage for MOCVD.

External Collaborations:

To provide laser/material interaction measurement, film growth, and modeling support, collaborations have been developed with the following individuals and groups: R. Revay, ETOM and Dr. A. Pique, Neocera and NRL for studies of metal sulfide films for optical data storage technology; Dr. P. Ghosh, Indian Institute of Technology, Kanpur, India for Monte Carlo vapor transport model development; Dr. M. Joseph, Indira Gandhi Institute, Kalpakkam, India for laser vaporization mass spectrometry and Dr. C. Chatillon, ENSEEG Recherche LTPCM, France for development of methods and data for quantifying mass spectrometric data (IUPAC sponsorship). In addition, information on laser-materials interaction phenomena have been provided to Dr. B. Siu,

Simpex Technologies for development of a new measurement approach to test microelectronic lead connects.

Planned Outcome:

This project will develop *in situ* measurement methods and process models for real-time analysis of the details of the deposition process during PLD and for other deposition processes such as MOCVD. Reference films, produced under well controlled conditions, to be used by others for film property measurement development, will also result from this work.

Accomplishments:

- A novel, real time, particulate reduction method based on deflection by a pulsed gas jet, timed to coincide with the appearance of the particulates prior to deposition (PLD), has been demonstrated. This method is still being optimized, but the feasibility has already been confirmed for at least a 90% reduction in the number of particulates reaching the substrate using $BaTiO_3$ targets. Manufacturers of PLD equipment and PLD films have expressed an interest in using this particulate control method (Neocera, PVD). Control of particulates produced during processing remains a significant technical barrier to the commercial utilization of PLD and to the efficient industrial application of MOCVD.

- By monitoring the PLD-produced plumes of SrS targets mass spectrometrically, we have been able to optimize the laser fluence and wavelength process conditions to yield desirable S-rich vapor compositions. This approach should allow for PLD of films without addition of H_2S, which is normally required for S-enrichment but is less desirable due to toxicity, corrosion, and other process control concerns. This work is part of a CRADA collaboration with ETOM an ATP awardee to demonstrate the feasibility of producing, by PLD, SrS-based optically active thin films with potential application as electron trapping optical storage, next generation compact discs.

- During the past year, we developed an optical absorption spectroscopic technique for measurement of vapor phase Ba and Ti atoms during PLD of $BaTiO_3$ thin films. The results, including both the relative amounts of Ba and Ti present in the gas phase during deposition, and the time, velocity, and spatial dependence of these species, were used to test gasdynamic models of the plume transport process. It is anticipated that a similar measurement approach can be used for planned MOCVD depositions (in collaboration with D. Kaiser).

- A two stage hydrodynamic PLD model was modified to describe the unsteady isothermal expansion of the high density vapor/plasma formed during the laser pulse, and to describe the abrupt transition of the gas flow to an adiabatic expansion at the end of the laser pulse in the presence of added process gases. A parameter was also introduced to the model defining the point of transition from a continuous flow to free flight where the velocity of the plume's outer edge becomes "frozen." Input parameters used in the model include the measured size of the laser spot at the target, the initial process gas pressure, the maximum effective surface temperature of the target and ejected vapor, and a temperature parameter

describing the plasma which forms above the target surface. Results from the model compare favorably to experimental results acquired using our various *in situ* monitoring techniques: *i.e.*, time-of-arrival profiles, plume images, and both emission and absorption spectroscopic data as a function of both time and position. The model shows that the rate of plume expansion in PLD is highly dependent upon the plasma temperature above the target surface. In a corollary effort, a Monte Carlo model has been developed that uses stochastic sampling with direct computation of molecular collisions to follow a selection of the multiple species in the gas plume as "tracers" of the gas flow. The results of this model reproduce quite well the detailed velocity profiles measured downstream by MBMS.

- During the past year, the PLD modeling activity was expanded to include processes occurring at the deposition plane, both within the gas and at the film-gas interface. The modeling approach consists of two parts. The first part implements a two dimensional Direct simulation Monte Carlo model that describes the collisional interaction between the plume species and a background gas in the presence of a surface held at a constant temperature different from that of the gas. Preliminary results indicate formation of a high temperature, high pressure gas boundary above the substrate. Gas flow images across the substrate were also developed. This steady state model is currently being modified to simulate the unsteady flow of laser-induced plumes, and the subsequent interaction within these plumes that we have observed spectroscopically. The second part of the gas-surface model seeks to simulate actual film growth. The modes of growth have been shown to be dependent on the interaction energies between the atoms.

Publications:

"Monte Carlo Simulations of Plume Evolution From Laser Ablation of Graphite and Barium Titanate," J.W. Hastie, D.W. Bonnell, A.J. Paul, P.K. Schenck, P.K. Ghosh, A. Ranjan, S. Sinha, IXth IUPAC Intl. Conference on High Temperature Materials Chemistry, Ed. K.A. Spear, (Electrochem. Soc, Pennington, N.J., 1997) - In press, 1997

"High Temperature Chemistry of the Pulsed Laser Thin Film Deposition Process," J.W. Hastie, A.J. Paul, D.W. Bonnell, P.K. Schenck, IXth IUPAC Intl. Conference on High Temperature Materials Chemistry, Ed. K.A. Spear, (Electrochem. Soc, Pennington, N.J., 1997) - In press, 1997

"Vaporization thermodynamics of KCl. Combined Processing of Total Vapor Pressure and Evaporation Rates," E.B. Rudnyi, D.W. Bonnell, J.W. Hastie, J. Phys. Chem. Ref. Data, Submitted 1997

"Particulate Reduction In the Pulsed Laser Deposition of $BaTiO_3$ Thin Films," P.K. Schenck, M.D. Vaudin, D.W. Bonnell, J.W. Hastie, and A.J. Paul, Appl. Surf. Sci., Submitted, 1997.

"Monte Carlo Simulations of Plume Evolution From Laser Ablation of Graphite and Barium Titanate," Amit Ranjan, Sanjeev Sinha, P.K. Ghosh, J.W. Hastie, D.W. Bonnell, A.J. Paul, & P.K. Schenck, Chem. Phys. Lett., in press, 1997.

"Processing and Characterization of Compositionally Modified $PbTiO_3$ Thin Films Prepared by Pulsed Laser Deposition," B.W. Lee, L.P. Cook, P.K. Schenck, W. Wong-Ng, C.K. Chiang, P.S. Brody, K.W. Bennett, in press J. Mater. Res., 1997.

"Influence of the Microstructure of Pt/Si Substrates on Textured Growth of Barium Titanate Thin Films Prepared by Pulsed Laser Deposition," C.S. Hwang, M.D. Vaudin, P.K. Schenck, in press J. Mater. Res., 1997.

PROGRAM TITLE: Thin Film Measurements and Standards

PROJECT TITLE: Optical Characterization Techniques

Principle Investigators: Lawrence H. Robins and Lawrence D. Rotter

Technical Objective:

The objective is to develop and to apply optical characterization techniques for the measurement of technologically important properties of ferroelectric oxides, wide-bandgap semiconductors, phosphor memory films, and related thin film systems of interest to the photonics and electronics industries.

Technical Description:

The project involves the use of Raman spectroscopy, cathodoluminescence (CL) imaging and spectroscopy, photoluminescence (PL), spectrophotometry, second harmonic generation (SHG), polarimetry, and prism coupling to determine thin film and substrate properties such as thickness, optical constants, electro-optic constants, waveguiding losses, electronic energy gap, defect and impurity energy levels, structural phase content, residual stress/strain, internal electric fields, and ferroelectric poling efficiency.

External Collaborations:

Joint investigation is in progress with Dennis Wickenden of Johns Hopkins University Applied Physics Laboratory of the group III nitrides. We are working with Don Lucca of Oklahoma State University and Eagle-Picher Corp. to investigate ultrafine diamond turning as a surface finishing method for II-VI single crystal substrates (CDs and ZnSe). Collaboration has begun with ETOM Technologies to study the properties of a class of doubly rare earth doped phosphors to be used for data storage.

Planned Outcomes:

A spectrophotometric technique suitable for routine use in an industrial setting will be developed to determine the amorphous content of $(Ba_{1-y},Sr_y)_xTiO_{2+x}$ and related films. A technique based on SHG will be developed to determine the presence and source of internal electric fields in $(Ba_{1-y},Sr_y)_xTiO_{2+x}$ and related films.

Spatially resolved CL will be used to measure the full depth of the subsurface damage regions that extend more than 2 μm beneath the surface in surface finished II-VI substrates.

Spatially resolved CL will be used to evaluate inhomogeneity and phase separation in $Ga_{1-y}In_yN$ films and quantum wells and to characterize the electronic structure of III-nitride films grown by lateral epitaxial overgrowth.

Accomplishments:

We have found a strong correlation between the volume fraction of crystalline material, f, and x in $(Ba_{1-y},Sr_y)_xTiO_{2+x}$ films that suggests that 1-f is a useful indicator of the amorphous content of these films. In films with $x<1$, an amorphous phase either coexists with a crystalline phase or comprises the entire film. For a series of films grown on MgO and fused quartz substrates by metal-organic chemical vapor deposition, the stoichiometry x was determined by wavelength dispersive spectrometry (WDS), and optical transmission spectra were obtained in the wavelength range 0.33 μm to 2.5 μm. The effective medium was assumed to consist of a single crystalline phase with a columnar structure embedded in a single amorphous phase. For films with x=1.01 (0.34), only a crystalline (amorphous) phase appeared in x-ray diffraction. The only variable parameter of the effective medium fit was f.

Raman spectroscopy was used to probe the phase content of $(Ba_{1-y},Sr_y)_xTiO_{2+x}$ films, in both the $x<1$ and $x>1$ ranges (determined by WDS, as above). Variations in spectral features were strongly correlated with x. A broad peak at high wavenumber (higher than any of the Raman lines of tetragonal $BaTiO_3$), which was seen only for $x<1$ and increased in intensity with decreasing x, is attributed to the Ti rich amorphous phase. A narrow, intense line at very high wavenumber, which was seen only for $x>1$, is attributed to a Ba rich crystalline phase such as Ba_2TiO_5. A 306 cm^{-1} line, which is a prominent feature of the Raman spectrum of single crystal and bulk ceramic $BaTiO_3$, was narrowest and most intense for the stoichiometric (x=1.01) film.

We have succeeded in depositing interdigitated electrodes on $(Ba_{1-y},Sr_y)_xTiO_{2+x}$ thin films using photolithographic liftoff. Using these electrodes we have observed the Curie transition in a $(Ba_{1-y},Sr_y)_xTiO_{2+x}$ thin film (by measuring its capacitance versus temperature) for comparison with the temperature dependence of the SHG in the same film. Continued studies of this nature should help elucidate the connection between the observed SHG and internal electric fields in these films.

$Al_xGa_{1-x}N$ films with x=0 to x=0.36 were characterized by CL imaging and spectroscopy and PL spectroscopy. Spatially resolved CL spectra taken from the vicinity of the microcracks and hexagonal defects show peak shifts, which we currently attribute to changes in the residual stress near the defects. We have also observed extra sub-bandgap peaks, which are attributed to localized states. PL spectra were obtained from the top surfaces and the film-substrate interfaces of several films. The interface PL spectra of some films show an extra peak 0.15 eV to 0.45 eV below the bandgap, which is ascribed to structural defects or impurity phases that occur near the interfaces. CL imaging and conventional optical microscopy reveal two types of morphological defects: networks of lines parallel to a threefold crystal symmetry direction, which are probably microcracks, and hexagonal-to-circular raised areas. The hexagonal defects occur only in the lower-x films, while the density of microcracks is greatest in the higher-x films.

CDs single crystals with surfaces prepared by chemical etching, chemomechanical polishing, and mechanical polishing with 0.25 μm particles, were characterized by depth resolved CL spectroscopy. The penetration depth was controlled by varying the incident electron energy. A deep level peak at 1.7 eV that was present in the spectra of the 0.25 μm mechanically polished specimen, but not the other specimens, is ascribed to defects created during polishing. The intensity ratio of the 1.7 eV

peak to other spectral features was highest at the maximum penetration depth of about 2 μm. This observation suggests that the depth of the subsurface damage region is significantly greater than 2 μm, and that a modification to the experimental technique, such as examination of cross-sectioned specimens, will be needed to probe the full extent of the damaged region.

Publications:

L.H. Robins, J.R. Lowney and D.K. Wickenden, "Cathodoluminescence, photoluminescence and optical absorbance spectroscopy of aluminum gallium nitride ($Al_xGa_{1-x}N$) films", submitted to J. Mater. Res.

L.H. Robins and J.A. Tuchman, "Photoluminescence studies of Sm^{2+} in the stimulable phosphor SrS:Eu,Sm", submitted to Phys. Rev. B

L.H. Robins and D.K. Wickenden, "Spatially resolved luminescence studies of defects and stress in aluminum gallium nitride films", submitted to Appl. Phys. Lett.

L.D. Rotter and D.L. Kaiser, "Detection of internal electric fields in $BaTiO_3$ thin films by optical second harmonic generation," submitted to J. Appl. Phys.

PROGRAM TITLE: Thin Film Measurements and Standards

PROJECT TITLE: Phase Determination Using EXAFS

Principal Investigator: Charles Bouldin

Technical Objective:

The purpose of this work is to provide U.S. industry with advanced x-ray characterization methods for evaluating materials used in photonic applications. X-ray measurement facilities are to include both x-ray absorption and resonant x-ray diffraction using synchrotron radiation.

Technical Description:

A number of technologically important photonic materials are prepared as thin films on a variety of substrates. It is often desirable to perform the deposition process using the lowest practical substrate temperature. Due to the low substrate temperatures and variation in the stoichiometric control during deposition, the films often contain unknown minority phases or amorphous components that can adversely alter the desired film properties through residual stress formation, light scattering, degradation of transport properties or other mechanisms. These unintended phases, particularly thin amorphous materials, are difficult to detect using standard characterization tools. In addition, thin films (10 nm to 100 nm) are likely to suffer some distortion from deposition on lattice-mismatched substrates. A combination of x-ray absorption fine structure measurements, conventional and resonant x-ray diffraction measurements are used to study the phase composition of thin film photonic materials.

External Collaborations:

Extended x-ray absorption fine structure (EXAFS) has been applied to several materials systems to determine variations in structure and composition. This work has been done in collaboration with City University of New York, University of Washington, Johns Hopkins University, Texas Instruments and Samsung.

Planned Outcomes:

Through use of the synchrotron at Brookhaven and the Advanced Photon Source at Argonne, the nearest and next-nearest neighbor environments associated with dopants in the thin films will be determined. This information is essential for a basic understanding of dopant behavior in these materials. These studies will also provide information regarding location of second phase material components.

Accomplishments:

Additional phases have been detected in barium titanate and strontium barium titanate films. These phases are detected by modeling the EXAFS data as a linear combination of spectra taken from

known reference materials such as TiO_2, bulk $BaTiO_3$ and Ba_2TiO_4. Preliminary measurements have shown that films that are Barium rich, i.e. the ratio of (Ba+Sr)/Ti > 1, contain a mixture of $BaTiO_3$ and Ba_2TiO_4. When the (Ba+Sr)/Ti ratio is nearly two, the films are nearly 100% composed of Ba_2TiO_4. EXAFS makes this phase identification very clearly, even though the x-ray diffraction shows only very weak Ba_2TiO_4 peaks. Despite the expectation from earlier diffraction measurements that the barium titanate and strontium barium titanate films contain "amorphous" phases, the evidence to date favors the existence of atomically well ordered off-stochiometry phases such as Ba_2TiO_4 and TiO_2; these phases appear very faintly in x-ray diffraction because of disorder or nano-size effects in grain growth.

Publications:

Co-Refinement of Diffraction Anomalous Fine Structure Data, M.G. Newville, J.O. Cross, L.B. Sorensen, C.E. Bouldin, in press, Nuclear Instruments and Methods, (1997).

On the Way to Understanding the Role of Platinum in a Pt-Zeolite Catalyst, D. Sayers, H. Renevier, J.L. Houdeau, J.F. Berar, J.M. Tonnerre, R. Raoux, A. Chester, D. Bazin, and C.E. Bouldin, European Synchrotron Radiation Facility Newsletter, January, 1997 issue, pg. 18.

Extended X-ray Absorption Fine Structure Study of Al(x)Ga(1-x)N Films Grown by Metalorganic Chemical Vapor Deposition, K.E. Miyano, J.C. Woicik, L. Robins, C.E. Bouldin, and D.K. Wicekenden, Applied Physics Letters, Vol. 70, 2108 (1997).

The Surface Structure of Cadmium Selenide NanoCrystallites, Adrian Carter, C.E. Bouldin, M.I. Bell, K. Kemner and S. Majetich, Phys. Rev. B, Vol. 55, 13822 (1997).

PROGRAM TITLE: Thin Film Measurements and Standards

PROJECT TITLE: Texture Measurements and Effects

Principal Investigator: Mark D. Vaudin, John Blendell, and Edwin R. Fuller

Technical Objectives:

The objectives of this work are to develop the tools to provide quantitative evaluation of local and global texture in thin films and to develop an understanding of how texture is developed and controlled during film processing.

Technical Description:

Crystallographic texture affects optical, electronic, and thermal properties of materials. For thin film geometries, in which dimensions in one direction are orders of magnitude smaller than those of the other two directions, texture can become a dominant factor in the success or failure of a films system to function. However, tools to measure texture, globally or locally, are only now being developed and factors that control texture in films remain largely unknown. To address the issues of texture measurement and control, we have adopted the following strategy. Using bulk materials as model systems, e.g., high T_c superconductors and alumina, measurement and analysis procedures have been developed: x-ray diffraction (XRD) for average texture evaluation, electron backscatter for individual grain orientation determination, and maximum likelihood statistical sampling technique to evaluate uncertainties in the evaluated texture. Now, we are applying these tools to investigate texture formation in thin ferroelectric films. Using the atomic force microscope (AFM) as well as x-ray diffraction and electron microscopy, we evaluate the texture and microstructure of substrates before and after deposition of barium titanate or barium strontium titanate films. The film texture is then correlated with substrate morphology, deposition temperature and deposition environment to determine what factors affect final film texture. The issue of how film texture is affected by these properties will then be addressed.

External Collaborations:

American Superconductor Corporation (ASC), John Bingert at Los Alamos National Labs, and John Gannon at Ohio State University have provided high T_c material and complementary measurements. Matthew Seabaugh at Penn State University is providing highly textured alumina specimens and doing independent characterization.

Planned Outcomes:

This work should provide industry with both a measurement procedure to obtain fast, accurate texture measurements using conventional powder x-ray diffractometers and a software package by which the accuracy of the measurements can be evaluated.

Accomplishments:

As part of the measurement development process;

- software packages for both Windows95 and DOS have been developed to perform the intensity correction calculations and provide the user with texture data in the form of corrected rocking curves.

- corrected rocking curves have been obtained from untextured alumina (SRM 676) and have shown no preferred orientation, thus showing that the technique is valid. This is a sensitive test in that any systematic errors in the experimental or theoretical approach will result in obvious deviations from a constant intensity level in the corrected rocking curves.

- data obtained with the rocking curve technique from $Bi_2Sr_2Ca_2Cu_3O_{10}$ superconducting tape specimens provided by American Superconductor Corporation have been compared with texture data obtained with a four-circle diffractometer by John Bingert at Los Alamos and found to match well. The technique has been successfully transferred to American Superconductor Corporation. Corrected rocking curves obtained from the same 2223 specimens at the two sites were experimentally indistinguishable.

- for small data sets of grain orientations (N<100), the maximum likelihood approach was shown to give a more accurate analysis of uncertainty than the alternative of binning the data into a histogram.

- applying the measurement techniques to films systems, we have determined that texture of a $BaTiO_3$ film deposited on a $Pt/TiO_2/SiO_2/Si$ substrate with strong $(111)_{Pt}$ texture by XRD is bimodal (001)/(111). Characterization with TEM showed (111) Pt/ $BaTiO_3$ epitaxy on "rough" Pt surfaces, and a (100) growth habit on planar (111) Pt facets. This behavior was explained in terms of the electrostatics of the perovskite lattice.

Publications:

"A Method for Crystallographic Texture Investigations Using Standard X-ray Equipment," Mark D. Vaudin, Martin W. Rupich, Martha Jowett, G.N. Riley and J. F. Bingert, submitted to J. Mat. Res.

"Comparison of Texture Measurement Techniques in Highly Oriented Liquid Phase Sintered α-Al_2O_3," M.M. Seabaugh, G. L. Messing, J. P. Cline and M.D. Vaudin, in preparation.

"Effect of Processing Parameters on the Degree of Orientation and Textured Fraction in Liquid-Phase-Sintered α-Al_2O_3," M. M. Seabaugh, J.P. Cline, M.D. Vaudin, and G.L. Messing, in preparation.

"Influence of Pt-based electrode surface on the textured growth of $BaTiO_3$ thin films by pulsed laser deposition", Cheol Seong Hwang, Mark D. Vaudin and Peter K. Schenck, accepted by J. Mater. Res.

PROGRAM TITLE: Thin Film Measurements and Standards

PROJECT TITLE: Thermal Measurement Development

Principle Investigators: Albert Feldman, Eduardo Gonzalez, and Grady White

Technical Objective:

The objective of this work is to develop measurement techniques that accurately and precisely measure the thermal diffusivity of films and, subsequently, to transfer these new techniques to industry. Included in the technique development are modifications of current models, as needed, and the organization of multilaboratory experiments to evaluate reproducibility and accuracy of the measurement processes.

Technical Description:

Thermal measurements are currently being made using two A.C. techniques: photo-thermal deflection and infrared (IR) radiometry. For both types of measurements, an amplitude modulated Ar^{+} laser is focussed onto the specimen surface to provide a periodic heat source. In the photo-thermal deflection measurement, a second, HeNe, probe laser beam is passed through the heated air adjacent to the specimen, and the refraction of the probe is measured. In contrast, the IR radiometry measurement uses an IR detector to monitor the heat generated in the film directly. In both experiments, the measured signals are functions of the thermal diffusivity values in the films and the substrate as well as of any thermal resistance at the film/substrate interface.

Models describing the IR radiometry results are being modified to incorporate effects due to different specimen and heating spot geometries. Analysis of the photo-thermal deflection experiment is being modified to include microstructural features of the specimens, e.g., texture, pore size and morphology, and grain size.

External Collaborations:

Toshiba and Dow Chemical are looking at aluminum nitride substrate materials. Materials Modification Inc. is investigating the thermal properties of plasma sprayed copper and copper/molybdenum specimens ultimately used for heat sink applications.

Planned Outcomes:

Two planned outcomes are associated with this work: the development of measurement methods to accurately determine the thermal diffusivity of thin films and film systems and the transfer to industry of the measurement technique and standardization procedures by which industry can have confidence in their measured values.

Accomplishments:

An international workshop, Thin Film Thermal Conductivity Measurement, was held as part of the 13th Symposium on Thermophysical Properties at the University of Colorado. At the discussion session, all of the participants recognized that large discrepancies in measured values of thin film thermal diffusivity occur between laboratories. Over 90% of the participants agreed to participate in round robin tests to assess potential thin film standard reference materials and potential measurement techniques and to attend future workshops to address the questions of insuring accuracy and reproducibility.

We have demonstrated that the photo-thermal deflection technique can measure changes in thermal diffusivity in bulk specimens resulting from porosity, crystallographic texture, and crystallization events. For example, we have recorded thermal diffusivity values ranging from 0.037 $cm^2 \cdot s^{-1}$ to 0.14 $cm^2 \cdot s^{-1}$, for samples with 38% and 0% volume fraction of porosity, respectively. The thermal diffusivity varies linearly with the volume fraction of porosity.

We have determined that the thermal diffusivity of polycrystalline samples of Bi_2Te_3 varies with the degree of crystallographic texture. We have recorded differences in thermal diffusivity greater than 35% between samples with no texture and those that are highly textured. In our work with Mo/Al_2O_3 40 bilayer composite films, we have determined that the thermal diffusivity of the composites increases from 0.004 $cm^2 \cdot s^{-1}$ to 0.024 $cm^2 \cdot s^{-1}$ when the samples are heat treated at high temperatures. Observations also indicate that the ratio of the heat flow across the layers to the heat flow in the plane approaches one as the specimens are heated. These changes appear to be related to the densification and crystallization of the Al_2O_3 layers. We have also studied the crystallization sequence of alumina films on substrates. The thermal diffusivity of these specimens changes from 0.0035 $cm^2 \cdot s^{-1}$ for an amorphous film to 0.023 $cm^2 \cdot s^{-1}$ for a crystalline film with a complex microstructure. In collaboration with industry, we have evaluated the thermal properties of plasma sprayed Cu and Mo/Cu composites prepared under conditions that can produce different microstructures. In summary, the results from this work on bulk specimens and films have suggested that the most prominent microstructural features that can affect thermal transport from most relevant to least relevant are: (1) porosity (relative density), (2) crystallinity, (3) texture, and (4) interface effects.

Work has begun to incorporate the topic of thermal measurements as a new measurement issue to be address by the international, pre-standards organization, VAMAS.

OTHER PROGRAMS

PROGRAM TITLE: Other

PROJECT TITLE: Characterization of Cements

Principal Investigator: Andrew J. Allen

Technical Objectives:

The objective of this research is to characterize microstructure evolution during hydration in cements, to determine what aspects of the microstructure relate most directly to performance, to characterize microstructure degradation due to environmental effects, and to probe the effects of additions of silica fume, fly ash, and other additives that may lead to superior performance.

Technical Description:

This project makes use of ultra-small-angle x-ray scattering (USAXS) and small-angle neutron scattering (SANS) to characterize microstructural evolution during the hydration of cements, as a function of environmental effects and additives, as it affects highway infrastructural concretes. Silica fume is a microsilica by-product of silicon and silicon-steel manufacture. It is increasingly being used as a cheap additive in cement and concrete, where it can (but does not always) enhance cement and concrete durability. Several silica fume slurries have been studied using USAXS, from which the silica fume particle size distributions have been determined. At the largest size range accessible with USAXS, the data indicate the presence of coarse agglomerates larger than one micrometer in size. Variations in the level of agglomeration have been explored as the main differentiating characteristic of the fumes. In addition, fundamental SANS studies have been carried out to explore the nature of the solid/pore interface in cements, since surface area is becoming an increasingly recognized predictor of cement and concrete properties.

External Collaborations:

R.A. Livingston, Federal Highway Administration, McLean monitors this program and is involved in interpretation of the USAXS and SANS measurements. J. Thomas and H.M. Jennings, Northwestern University, collaborate with the Ceramics Division on the surface area characterization of hydrating cements utilizing SANS as the primary characterization technique.

Planned Outcome:

Out of these studies is expected a quantitative assessment of how the microstructures of hydrating cement systems can be controlled by the hydration conditions and by the use of cement additives. Manufacturers should be able to use this cement and concrete information to obtain microstructures leading to optimum strength and durability.

Accomplishments:

A semi-fractal microstructural model of the hydration of cement systems has been used to develop

further our understanding of the link between the degree of low density agglomeration in silica fume additives, and possible deleterious microstructural effects that can develop during the hydration of cement blends incorporating such fumes.

The USAXS studies have enabled us to determine the particle size distributions within silica fume slurry suspensions. The volume weighted size distributions showed that most of the particles were larger than 10 nm but smaller than 300 nm. Derived from these broad volume weighted size distributions, the number weighted size distributions (as would be determined, for example, by SEM particle counting methods) are strongly peaked at ~ 25 nm diameter, and show virtually no variation among the fumes. Despite the broad range of particle sizes present in the volume weighted distributions, absolute volume fraction and surface area (Porod scattering) measurements indicate well dispersed fumes with surface areas per unit mass of silica ~ 40,000 m^2Kg^{-1}. Both in the size distributions and in the USAXS data itself, there is evidence of a much coarser component of at least several micrometers in size. This observation has been confirmed by preliminary laser particle size analysis (Lin-Sien H. Lum, Ceramics Division), which indicates an ensemble distribution in the 5 μm to 50 μ m diameter range. The larger features are believed to be low density, stable agglomerates of the silica particles already included in the main USAXS size distributions. While these basic attributes of silica fume are known from other work, the USAXS studies have allowed the degree of low density agglomeration to be quantified.

By estimating the coarse surface area from the additional Porod scattering component observed at the smaller USAXS scattering vectors studied for each fume, and comparing this with the total surface area deduced from the main Porod regime at high scattering vectors, it has been possible to quantify the total surface area of this low density agglomeration. Unlike the basic particle size distributions, the tendency to form low density agglomerates was found to differ considerably among the fumes. SANS studies, of the microstructural evolution during the hydration of cements blended with these very fumes, have shown that the degree of low density agglomeration is linked with a deleterious microstructure development in the hydrating cement blends. The major implication of this work is that silica fumes can be improved to a quantifiable degree by processing to break up the large, low density agglomerates prior to their incorporation in cements.

In parallel with this work, a SANS investigation has been undertaken of the nature of the pore/gel interface in cement systems. Measurement of the internal surface area of cements is of importance because it is related to permeability and expansion effects in concrete, and hence to associated long-term mechanical properties and durability. Concentrating initially on reconciling various disparate measures (by a range of methods) of the internal surface area in cement, these studies are becoming focussed on the possible coexistence of two different morphologies of the principal microstructural product of a cement hydration: the calcium-silicate-hydrate (C-S-H) gel. One of these morphologies has a high internal surface area, measurable by SANS, the other, a high density form, does not. By a series of experiments have been exploring the effects of water-to-cement ratio, temperature, age, and other hydration conditions, these studies are establishing that the high surface area form of C-S-H adjusts its morphology to fit the available space, and that this is the main agent binding the cement grains together. The dense C-S-H form manifests itself in other ways, and its formation may dominate the hydration reactions after the first 24 hours. These studies may offer some explanation of why, for example, the development of cement and concrete properties is frequently not easily

related to the degree of hydration, as measured (in thermal calorimetry) by the heat output of the hydration reactions.

Publications:

J.J. Thomas, H.M. Jennings and A.J. Allen, "Determination of the Neutron Scattering Contrast of Hydrated Portland Cement Paste using H_2O/D_2O Exchange," Advanced Cement-Based Materials, in press. (1997).

J.J. Thomas, H.M. Jennings and A.J. Allen, "The Surface Area of Cement Paste as Measured by Neutron Scattering - Evidence for Two C-S-H Morphologies," Cem. Concr. Res., in press. (1997).

A.J. Allen and R.A. Livingston, "The Relationship Between Differences in Silica Fume Additives and the Fine Scale Microstructural Evolution in Cement-Based Materials," Advanced Cement-Based Materials, in press. (1997).

PROGRAM TITLE: Other

PROJECT TITLE: Modeling of Phase Transitions

Principal Investigators: B. P. Burton and R. P. McCormack

Technical Objectives:

This research is designed to assist industry by elucidating the role of order-disorder phenomena in determining the phase relations and physical properties of certain technologically important ceramic materials.

Technical Description:

Typically, the ferroelectric, dielectric, magnetic, or transport properties of these materials are sensitive functions of the state of cation order. Therefore, First-Principles Phase Diagram (FPPD) calculations are used to predict cation ordering phenomena, and critical experiments are performed to test the predictions. Additionally, performance tests are developed to benchmark various techniques for calculating the formation energies on which FPPD calculations are based.

External Collaborations:

- Collaboration with Jordi Fontan (Univ. Autonoma, Barcelona, Spain) on FPPD calculations of the NaCl-KCl, NaBr-KBr, and NaI-KI phase diagrams.
- Collaborations with G. Ceder (MIT) on issues related to Ising model calculations.
- Collaboration with Anna Roig (ICMAB, Univ. Autonoma, Barcelona, Spain) Mossbauer studies of magnetism, and iron in elevated valence states (Fe^{4+} , Fe^{5+}) in the system $BaTiO_3$-$Ba_2Fe_2O_5$.
- Application of the Vienna Ab-initio Simulation Package (VASP) pseudopotential code to calculate structure energies for FPPD calculations for ordered supercells in the system $Ba(Zn_{1/3}Ta_{2/3})O_3$, G. Kern, Techincal University, Vienna.
- Application of the self consistent atomic deformation (SSCAD) model to calculate structure energies for FPPD calculations for oxide systems, and the "isotropy" program for symmetry analysis, with H. Stokes (BYU), and L. Boyer (NRL).
- Collaboration with R. Selinger (Catholic U) on Monte Carlo calculations.

Planned Outcomes:

This research will predict ordering behavior in complex technologically important oxide systems, with the objectives of: (1) minimizing the experimental work necessary to elucidate their phase

relations; (2) perfecting theoretical techniques; (3) optimizing processing strategies for these materials; and (4) predicting the existence of new, technologically relevant ordered phases.

Accomplishments:

Both *ad hoc* and FPPD calculations were performed for the system $Ba(Zn_{1/3}Ta_{2/3}O_3$, and the calculated results qualitatively reproduced experimental data on the strongly first order character of the $P\bar{3}m_1$ to $Pm\bar{3}$ transition. SSCAD total energy calculations were performed for 70 different ordered supercells in the system $BaTaO_3$ - $BaZnO_3$ - $BaZrO_3$. Major results of these calculations were:

- Analysis of *ad hoc* Hamiltonians demonstrated that one can generate the 1:2 ground state that is observed in $Ba(Zn_{1/3}Ta_{2/3})O_3$ with a minimum of two effective cluster interactions. This result permitted the calculation of prototype phase diagrams that result from very simple, physically transparent models.

- SSCAD structure energies for 37 different possible ordered phases in the system $BaTaO_3$ - $BaZnO_3$ were used as a basis for FPPD modeling of the $P\bar{3}m$ to $Pm\bar{3}$ transition in $Ba(Zn_{1/3}Ta_{2/3})O_3$. The Hamiltonian that was fit to these total energies was used in a Monte Carlo calculation to simulate finite temperature order-disorder behavior in $Ba(Zn_{1/3}Ta_{2/3})O_3$.

- SSCAD structure energies for 70 different possible ordered phases in the system $BaTaO_3$ - $BaZnO_3$ - $BaZrO_3$ provided a database from which to make FPPD calculations for the quasibinary system $Ba(Zn_{1/3}Ta_{2/3})O_3$ - $BaZrO_3$.

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B.P. Burton, R.P. McCormack, B.H. Toby, and E.K. Goo, "Cation Ordering in Some ABO_3 Perovskites," Ferroelectrics 194, 187-206 (1997).

R. McCormack and B. Burton, Modeling Phase Stability in $A(B_{1/3}B'_{2/3}O_3$ Perovskites, Computational Materials Science, 8, 153-160 (1997).

R. McCormack and B. Burton, Modeling Phase Stability in $A(B_{1/3}B'_{2/3}O_3$ Perovskites, RS Proceedings, In press.

PROGRAM TITLE: Other

PROJECT TITLE: Materials for Wireless Communication

Principal Investigator: Terrell A. Vanderah

Technical Objectives:

Experimental studies are conducted to determine phase equilibria and structure-property relations in complex titanate-based systems having potential applications as dielectric oxides in wireless communications systems.

Technical Description:

Dielectric ceramics are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (e.g., resonators, bandpass filters, circulators). The required properties for the ceramic materials include high dielectric constant, minimal dielectric loss, and essentially zero temperature dependence of dielectric properties. Knowledge of phase equilibria relations is important because all ceramic components are processed as mixtures to achieve "compensation", i.e., a net overall zero temperature coefficient. The approach taken by the phase equilibria group emphasizes experimental determination of previously unknown ternary (or higher) oxide systems containing one or more components or compounds that exhibit useful properties as dielectric ceramics for microwave communications. Technical efforts include synthesis, structural analysis, determination of phase relations, and characterization (via collaborative efforts) of dielectric properties. Systems of current interest include $BaO:Fe_2O_3:TiO_2$, $SrO:TiO_2:Nb_2O_5$, $BaO:TiO_2:Ta_2O_5$, $SrO:TiO_2:Ta_2O_5$, $CaO:TiO_2:Ta_2O_5$, and $CaO:TiO_2:Nb_2O_5$.

External Collaborations:

Characterization of dielectric properties is accomplished by collaborations with UCLA (Electrical Engineering Department) and NIST staff in Boulder (Electromagnetic Fields Division). Active industrial collaborations exist with Lucent Technologies, Trans-Tech, Inc., and Trak Ceramics.

Planned Outcomes:

Accurate, experimentally determined phase diagrams will be available that are of immediate interest to U.S. industry involved in the production of ceramics for wireless communications systems. Diagrams that include dielectric property data will indicate the chemical identities of new, potentially useful compounds as well as the compositions of equilibrium mixtures that can be processed as ceramics with controlled properties.

Accomplishments:

Detailed characterization of new phases found previously in the $BaO:Fe_2O_3:TiO_2$ system has continued. Using single crystal and powder x-ray diffraction methods, the crystal structure of

$Ba_5Fe_4Ti_{10}O_{31}$ was determined and its magnetic and dielectric properties were measured. $Ba_5Fe_4Ti_{10}O_{31}$ crystallizes in space group *P6₃/mcm* (No. 193) (a=9.9886(2)Å c=42.226(2) Å, and exhibits an 18-layer close-packed structure built from vacancy-free [O,(Ba,O)] layers. The structure features octahedral sites occupied by a mixture of Fe^{3+} and Ti^{4+}, with some preferential ordering, and tetrahedral sites occupied by Fe^{3+}, one of which shares faces and is half occupied. Some Ba ions in the structure display (9+3) coordination with three unusually long Ba–O bond distances. Computation of bond valence sums about the cation sites using the observed bond distances reveals significant deviations from the valence sum rule, indicating that the structure of $Ba_5Fe_4Ti_{10}O_{31}$ contains residual strain not relieved by distortion. Indexed experimental x-ray powder diffraction data for $Ba_5Fe_4Ti_{10}O_{31}$ were prepared for the JCPDS database. The compound exhibits approximately paramagnetic behavior that deviates somewhat from the Curie Law. The relative permittivity and dielectric loss tangent were measured between 7.1 Ghz and 7.7 GHz, yielding values of 32 and $(3.3\pm0.3)x10^{-3}$, respectively, that were essentially independent of frequency. Detailed reference x-ray powder diffraction data were prepared for $Ba_2Fe_2Ti_4O_{13}$, $Ba_3Fe_{10}TiO_{20}$, and $Ba_4Fe_2Ti_{10}O_{27}$.

Experimental determination of the $SrO:TiO_2:Nb_2O_5$ ternary diagram is nearly complete. A series of incommensurately modulated $A_nB_nO_{3n+2}$ phases in the $SrTiO_3$-$Sr_2Nb_2O_7$ quasibinary system was found to display unusual and potentially useful dielectric properties. Members of the homologous series with n = 4, 5, 6, 7, and non-integer values between 4 and 5 were characterized by HREM/TEM, bulk x-ray powder diffraction, and capacitive measurements of relative permittivities and their temperature coefficients. The structures of these compounds feature distorted perovskite-like slabs sliced parallel to the cubic (110) plane. For members of the series found at integral values, n indicates the width of the slabs (in number of $[BO_6]$ octahedra, where B = Ti^{4+} or Nb^{5+}). Samples at non-integral values of n between 4 and 5 exhibited "line structures"; i.e., ordered intergrowths of the n=4 and n=5 structures. For these samples, n indicates the *average* width of the perovskite-like slabs. The compounds share a basic orthorhombic unit cell with $\boldsymbol{a} \approx 3.9$ Å, $\boldsymbol{c} \approx 5.6$ Å, and a long $\boldsymbol{b}$-dimension that increases incrementally as the width of the slabs increases. High resolution electron microscopy indicated that all of the compounds are incommensurately modulated along the shortest 3.9 Å cell dimension. These effects were not apparent in the bulk x-ray powder diffraction patterns. Experimental reference x-ray powder patterns were prepared for the new compounds with n = 4.33, 6, and 7; i.e., $Sr_{4.33}Ti_{0.33}Nb_4O_{15}$, $Sr_6Ti_2Nb_4O_{20}$, and $Sr_7Ti_3Nb_4O_{23}$. Preliminary capacitive measurements from 100 Hz to 5 MHZ indicated that all of the compounds exhibit relative permittivities that are dramatically lower than that of $SrTiO_3$ and somewhat higher than that of $Sr_4Nb_4O_{14}$. The addition of Nb^{5+} to $SrTiO_3$ causes a much more drastic change in dielectric constant than the addition of Ti^{4+} to $Sr_4Nb_4O_{14}$. The temperature coefficients were relatively small in magnitude and negative in sign except that of the n=6 member, which was found to be markedly larger and positive in sign. This result is unexpected given the crystal-chemical similarities of the series; further detailed studies at microwave frequencies are in progress at the Boulder laboratories.

Publications:

T.A. Vanderah, "Workshop on Materials and Measurements for Wireless Communications," J. Res. NIST **101**(6), 797-802 (1996).

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J. M. Loezos, T.A. Vanderah, and J.P. Cline, "New Ternary Compounds in the $BaO:Fe_2O_3:TiO_2$ System: $Ba_2Fe_2Ti_4O_{13}$ ("2:1:4"), $Ba_3Fe_{10}TiO_{20}$ ("3:5:1"), and $Ba_4Fe_2Ti_{10}O_{27}$ ("4:1:10")," Powder Diffraction, **12**(4), xxx (1997).

I.Levin, L.A. Bendersky, T.A.Vanderah, R.S. Roth, and O.Stafsudd, "A Series of Incommensurately Modulated $A_nB_nO_{3n+2}$ Phases in the $SrTiO_3$-$Sr_2Nb_2O_7$ Quasibinary System," Materials Research Bulletin, in press.

PROGRAM TITLE: Other

PROJECT TITLE: SRMs for Powder Diffraction

Principal Investigators: James P. Cline, Richard D. Deslattes and Jean-Louis Staudenmann (Physics Laboratory), Brian H. Toby (Center for Neutron Research)

Technical Objective:

The objective of this project is to develop Standard Reference Materials (SRMs) for use with x-ray powder diffraction measurements.

Technical Description:

In the most general sense, x-ray and neutron powder diffraction patterns consist of sets of intensity values measured over a range of crystallographic d-spacings. These patterns exhibit peaks which result from the interference of that portion of the incident radiation that is scattered coherently from the periodic crystal structure of the specimen. The form of the pattern depends on the qualitative, quantitative, crystallographic, and microstructural aspects of the sample. Therefore, proper analysis of diffraction patterns can provide considerable information about the specimen, giving rise to a wide range of applications for this technique.

The three variables associated with diffraction equipment which can be evaluated with NIST powder diffraction SRMs are: 1) the d-spacing or line position, 2) line intensity as a function of position, or instrument sensitivity, and 3) instrumental and sample contributions to the shape of reflection profiles. Additional powder diffraction SRMs are designed for quantitative analysis with the use of the internal standard method.

We are presently pursuing a new generation of line position SRMs which will be certified *via* a robust linkage to the iodine stabilized HeNe laser length standard. This project has involved the construction of a diffractometer capable of measurement accuracy to the parts per million range. In order to accomplish this, the machine has several unique features: A dual mirror optic that results in a parallel incident beam of high flux from a laboratory source, and an encoded goniometer capable of achieving sub-arcsecond accuracy and scanning symmetrically about the zero angle. These features permit measurements to be free from penetration and centration errors of the sample, and from zero errors of the goniometer. The silicon powder to be used for the SRM is being prepared from a dedicated production run of intrinsic material grown by the float zone method. The lattice parameter of the single crystal material has been verified to be uniform to a relative standard uncertainty of 0.000001%. The surface character of the powder is also being considered; the surface energy will result in stresses on the particles which will effect the measured lattice parameter.

The observed diffraction profile from the diffractometer consists of a sample profile convolved with an instrument profile and superimposed with noise. The sample profile characterizes the broadening due to crystallite size and microstrain effects within the sample. Although there exist several methods of determining the sample profile, they often require specific assumptions concerning the functional form of the sample profiles; otherwise the solutions may be ill-conditioned. The approach which has been developed to solve this problem is to apply the Maximum Entropy method (MaxEnt). The MaxEnt method incorporates the *a priori* information about the instrument profile and noise distribution as constraints and determines the solution which maximizes the entropy with respect to these constrains. At present, research work is concentrating on developing a generalized MaxEnt/Bayesian method which could be applied to deconvolving and separating overlapped profile peaks and which could be adopted for crystallite size and microstrain analysis.

Conventional methods of quantitative analysis are based on the Reference Intensity Ratio, RIR, method. A more accurate and precise method is Quantitative Rietveld Analysis, QRA, in which the powder diffraction data are analyzed with the Rietveld method. This method entails the calculation of the pattern from crystallographic, microstructural, and equipment characteristics which are represented parametrically in modeling functions. The difference between the calculated and observed pattern is then minimized by sequentially refining the parameters contained in model functions. The evaluated functions then constitute a quantitative description of the specimen. Both of these methods can be used to perform quantitative analysis without the use of an internal standard. However, in order to perform an accurate quantitative analysis which includes the amorphous content, a standard of known phase purity must be used. Thus, a major focus of the work in this area has been the development of a measurement and certification method for the amorphous content of SRM 676, a non-orienting alumina powder which is presently certified with respect to lattice parameters and eight relative intensity values.

The experimental approach is based on the comparison of the phase abundance of two phase mixtures determined from the preparation procedure using an analytical balance, which includes the amorphous component, to that determined from the diffraction data, which does not. Specimens consisted of 50-50 mixtures of SRM 676 and silicon powder, the latter material was obtained from crushed and jet milled single crystal, electronic grade boules. This microstructure allowed for the assumption that all amorphous material in the silicon powder was confined to a surface layer on the particles, and that the thickness of the layer was constant with respect to particle size. Thus, by systematically varying the surface area of the silicon powder, we could model its effect on the data. However, prerequisite to the success of this method was an unbiased measurement method. Potential for bias was judged from the plausibility of the refined results obtained from a number of powder diffraction methods. Data were collected *via* time-of-flight, TOF, and constant wavelength, CW, neutron powder diffraction, and synchrotron and conventional x-ray powder diffraction. Analysis of the refinements indicated that the TOF data were the least biased, and thus the amorphous content of the alumina was credibly determined.

External Collaborations:

Robert B. Von Dreele (Los Alamos National Laboratory), Walter Kalceff and Nicholas Armstrong (University of Technology, Sydney)

Planned Outcomes:

Certification of a new generation of line position SRMs with roughly an order of magnitude improvement in certainty of the certified lattice parameters will be completed with the new diffraction equipment. The MaxEnt/Baysian approach to profile deconvolution and analysis of particle size/microstrain induced profile broadening will be established. The certification of amorphous content in SRM 676 will be completed.

Accomplishments:

- A powder diffractometer capable of lattice parameter measurements to the parts per million range has been constructed.

- The amorphous content of SRM 676, alumina powder, has been determined to within a few tenths of a percent.

- The Maximum Entropy Method has been applied to the deconvolution of the x-ray diffraction line profiles for the determination of sample induced profile broadening. The effect of equipment optics on the observed position of profile maxima has been characterized and evaluated with a fundamental parameters approach.

PROGRAM TITLE: Other

PROJECT TITLE: X-ray Reference Powder Diffraction Patterns

Principle Investigators: Winnie Wong-Ng and James Kaduk

Technical Objectives:

The primary objective of this project is to determine x-ray reference powder diffraction patterns for important ceramic materials. These reference patterns are used to identify the phase components in research materials. A further objective is to develop a procedure for obtaining x-ray Rietveld reference patterns.

Technical Description:

X-ray powder diffraction is a powerful, non-destructive, and convenient technique for material characterization. When using this method, x-ray reference patterns (unique d-spacings and intensities) are used to serve as "finger prints" for phase identification. The conventional method of preparing an x-ray pattern involves the use of least-squares lattice refinements together with intensity values expressed as peak heights. In recent years, due to the advent of Rietveld refinement methods for powder diffraction data, powder patterns can be obtained by including information derived from known structural models. Also, during the refinement process, if cations with similar scattering power substitute for each other on the same crystallographic site, a combined refinement procedure using both the neutron and x-ray diffraction data can be used. In this way, the mixed site occupancy can be obtained with greatly improved accuracy. For our project, all data processing was carried out using the program suite GSAS (published by the Los Alamos National Laboratory). In all cases, the x-ray profiles were described by a pseudo-Voigt function, while the neutron profiles were described by a Gaussian function modified for peak asymmetry.

The materials included in this study emphasize technologically important ceramics, such as superconductors, ferroelectrics, microwave dielectrics, and engineering refractories, which have significant impacts on the ceramics industries.

Accomplishments:

A Rietveld pattern decomposition procedure for obtaining x-ray diffraction patterns has been established. With this procedure, the reported peak positions are calculated from the refined lattice parameters, which represent the best measure of the true positions.

Reference patterns were obtained using both the conventional method and the newly established procedure. Samples of several series of technically important materials that are related to high temperature superconductors and microwave materials were prepared, including $(Ca,Sr)_2PbO_4$, $Ba_4Ti_{10}Al_2O_{27}$, $BaSrRCu_3O_{6+x}$ (R=lanthanides), $Sr_{4+x}Ca_xPb_2O_8$, BaR_2ZnO_5, Rni2B2C, Bi_8SrCaO_x, and BaR_2PdO_5. X-ray powder diffraction patterns were prepared for most of these phases and will be included in the X-ray Powder Diffraction File (PFD).

External Collaborations:

This project was partially supported by the International Center for Diffraction Data (ICDD), a nonprofit organization that functions as a scientific organization as well as a publishing house for three crystallographic databases (PDF, NIST Crystal Data, and NIST/Sandia/ICDD Electron Diffraction Database). Collaborators on this project include James Kaduk of Amoco Research Laboratory, R.A.Young of the Physics Department of Georgia Institute of Technology, and B.Toby of the NIST Center for Neutron Research.

Planned Outcome:

When the Rietveld pattern decomposition procedure is employed, x-ray reference patterns can be prepared in an efficient and reliable manner. Since the availability of reliable diffraction references is essential to the application of the x-ray diffraction technique, patterns of technologically important materials produced as a result of this work will be an integral part of the PDF, and are expected to be widely used in industrial, academic and government laboratories.

Publications:

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RESEARCH STAFF

*The Ceramics Division Staff E-mail addresses can be accessed using the **fname.lname.@nist.gov**, except as otherwise noted. (Example: stephen.freiman@nist.gov)*

Allen, Andrew J. 301/975-5982	• Small angle x-ray scattering • Ceramic microstructure analysis
Begley, Edwin F. 301/975-6118	• Database management methods • Engineering database structures • Digital video interactive technology
Black, David R. 301/975-5976	• Defect microstructure in diamond • Polycrystalline diffraction imaging • X-ray imaging of photonic materials
Blendell, John E. 301/975-5796	• Ceramic processing and clean-room processing • Sintering and diffusion controlled processes • Processing high-T_c ceramic superconductors • Activation chemical analysis
Bonnell, David W. 301/975-5755	• Computer automation • Molecular-beam mass spectrometry • Thermodynamic modeling • Laser/plasma sputtering
Bouldin, Charles E. 301/975-2046	• X-ray absorption spectroscopy • Diffraction anomalous fine structure • GeSi heterojunction bipolar transistors
Braun, Linda M. 301/975-5777	• Raman stress measurements • Ceramic matrix composites • Toughening mechanisms
Burdette, Harold E 301/975-5979	• X-ray optics • X-ray diffraction imaging • Crystal growth • Instrumentation

Burton, Benjamin P. 301/975-6043	• Calculated phase diagrams • Dielectric ceramics
Carpenter, Joseph A., Jr. 301/975-6397	• Functional ceramics applications • Technical assessments • Industrial liaisons
Carter, W. Craig 301/975-3971 w.carter@nist.gov	• Materials thermodynamics • Advanced mathematical and computational techniques • Computation of materials processes
Cellarosi, Mario 301/975-6123	• Glass standards • Machining data
Chuang, Tze-Jer 301/975-5773	• Creep/creep rupture • Fracture mechanics • Finite-element modeling • Lifetime predictions
Clevinger, Mary A. 301/975-6109	• Phase diagrams for ceramists • Computerized data
Cline, James P. 301/975-5793	• Standard reference materials • High-temperature x-ray diffraction • Microstructural effects in x-ray diffraction • Rietveld refinement of x-ray diffraction data
Cook, Lawrence P. 301/975-6114 larry.cook@nist.gov	• High-temperature chemistry • Phase equilibria
Dapkunas, Stanley J. 301/975-6119	• Structural ceramics applications • Technical assessments • Coatings

Feldman, Albert 301/975-5740	• Thermal properties • Modeling thermal wave propagation • Thin-film optical properties
Fischer, Daniel A. 516/344-5177 fischer@x23a3df.nsls.bnl.gov	• X-ray absorption fine structure • X-ray scattering • Surface science
Freiman, Stephen W. 301/975-6119	• Electronic ceramics • Mechanical properties
Fuller, Edwin, R., Jr. 301/975-5795	• Influence of microstructure on fracture • Toughening mechanisms • Microstructural modeling and simulation
Gates, Richard S. 301/975-3677	• Tribo-chemistry • Surface chemical properties of ceramics
Gonzalez, Eduardo 301/975-6102	• Ceramic Processing • Nano-scale sintering • Texture analysis
Hackley, Vincent A. 301/975-5790 vince.hackley@nist.gov	• Electrokinetic and electroactive measurement • Slurry rheology • Surface chemistry of powders.
Hastie, John W. 301/975-5754	• High-temperature chemistry • Phase equilibria thermochemistry • Molecular-beam mass spectrometry • Thin-film deposition • Vapor deposition process control and modeling
Hockey, Bernard J. 301/975-5780	• Electron microscopy • High-temperature creep

Hsu, Stephen M. 301/975-6120	• Ceramic wear mechanisms • Engineered ceramic surfaces • Lubrication and machining of ceramics
Ives, Lewis K. 301/975-6013	• Wear of materials • Transmission electron microscopy • Machining of ceramics
Jahanmir, Said 301/975-3671	• Ceramic machining • Mechanisms of material removal • Mechanics of contacts • Effects of machining on mechanical properties
Harris, Joyce F. 301/975-6045	• Data acquisitions • Digitization and data entry
Kaiser, Debra L. 301/975-6759	• Ferroelectric oxide thin films • Physical properties and structures of high-temperature superconductors
Kelly, James F. 301/975-5794	• Quantitative scanning electron microscopy • Image analysis • Microstructure analysis • Powder standards
Krause, Ralph F., Jr. 301/975-5781	• Creep in flexure and tension • Fracture mechanics • Hot pressing • Chemical thermodynamics
Levine, Lyle 301/975-6032	• X-ray scattering • Defects structure in crystals

Long, Gabrielle G. 301/975-5975	• Small-angle x-ray and neutron scattering • Ceramic microstructure evolution as a function of processing • X-ray optics
Luecke, William 301/975-5744	• Creep/creep rupture • Mechanical test development
Lum, Lin-Sien H. 301/975-3674	• Powder characterization • Instrumental analysis
McGuiggan, Patricia M. 301/975-4599	• Microtribology • Surface force measurement
Minor, Dennis B. 301/975-5787	• Analytical scanning electron microscopy of ceramics and particulates • Powder test sample preparation • Powder characterization
Munro, Ronald G. 301/975-6127	• Materials properties of advanced ceramics • Data evaluation and validation • Analysis of data relations
Onoda, George Y. 301/975-4489	• Ceramic processing science • Physics of particulate materials • Characterization of powders
Paul, Albert J. 301/975-6004	• Laser physics • Plasma diagnostics
Pei, Patrick T. 301/975-3681	• Spectroscopic and thermal characterization • Chemical coating • Powders characterization

Quinn, George D. 301/975-5765	• Mechanical property test standards • Standard reference materials • Creep testing
Ravel, Bruce 301/975-5759	• X-ray analysis • Ferroelectrics
Robins, Lawrence H. 301/975-5263	• Defect identification and distribution • Cathodoluminescence imaging and spectroscopy • Photoluminescence spectroscopy • Raman spectroscopy
Roosen, Andrew J. 301/975-6166	• Microstructural modeling • Computer simulation
Rotter, Lawrence D. 301/975-6603	• Measurement of electro-optic coefficients • Photorefractive effect • Optical spectroscopy of thin films
Schenck, Peter K. 301/975-5758	• Emission and laser spectroscopy • Thin-film deposition • Computer graphics and image analysis • Laboratory automation • Plasma monitoring and control
Smith, Douglas T. 301/975-5768	• Surface forces • Charge transfer at interfaces • Adhesion and friction
Spal, Richard D. 301/975-4028	• X-ray optics • Diffraction physics • X-ray scattering
Steiner, Bruce W. 301/975-5977	• High-resolution diffraction imaging • Defects in monolithic crystals and multilayers • Non-linear optical processes

Vanderah, Terrell A. 301/975-5785	• Solid-state chemistry • Phase equilibria of microwave dielectrics
Vaudin, Mark D. 301/975-5799	• Electron microscopy • Microscopy and diffraction studies of interfaces • Computer modeling of grain-boundary phenomena • Dielectric films
Wallace, Jay S. 301/975-5984	• Mechanical test development • Ceramic coatings • Thermal analysis
Wang, Pu Sen 301/975-6104 pu.wang@nist.gov	• Solid-state nuclear magnetic resonance • Spectroscopic characterization
White, Grady S. 301/975-5752	• Thin films • Nondestructive evaluation • Subcritical crack growth • Stress measurements • Cyclic fatigue
Woicik, Joseph C. 516/344-5236 woicik@ssrl01.slac.stanford.edu	• UV photoemission • X-ray standing waves • Surface and interface science
Wong-Ng, Winnie 301/975-5791	• X-ray crystallography and reference patterns • Phase equilibria/crystal chemistry of high-T_c superconductors • Molecular orbital calculations

GUEST SCIENTISTS AND GRADUATE STUDENTS

Balzaretti, Naira	Institute de Fisica, Brazil
Bartlelt, Gunter	Federal Inst. of Materials Res. and Testing
Beck, Uwe	BAM
Boukari, Hacene	University of Maryland
Brower, Daniel	Optex Corporation
Cedeno, Christina	American Ceramic Society
Chen, Chun-I	Pennsylvania State University
Chen, Hailong	University of Tokyo
Cho, Unchung	University of Illinois
Cho, Wonoh	Korea Research Inst. of Technology
Chu, Steven	State University of New York at Stony Brook
Dong, Xiaoyua	University of Medicine & Dentistry of New Jersey
Fang, Hsu-Wei	University of Maryland
Farabaugh, Edward	Consultant
Fu, Zugen	State Univ. of N.Y. at Stony Brook
Greenwood, William	University of Maryland

Haller, Wolfgang	Abbott Laboratories
Hayward, Evans	American Ceramic Society
Hill, Michael	Trans-Tech Inc.
Hryniewicz, Piotr	University of Delaware
Ilavsky, Jan	State University of New York at Stony Brook
Jemian, Peter	University of Illinois at Urbana/Champaign
Jiang, Feng	University of Maryland
Job, Lenox	University of Maryland
Joseph, Mathew	India Gandhi Center for Atomic Research
Kailas, Satish	Indian Institute of Science
Kanematsu, Wataru	National Industrial Res. Inst. of Nagoya
Kauffman, Dale	Consultant
Kim, Myong-Ho	Chang-Won National University
Lee, Soo-Wohn	Sun Moon University
Lee, Yong Eui	Seoul National University
Levin, Igor	Israel Institute of Technology
Liu, Haiyan	University of Maryland
Loezos, John	University of Maryland

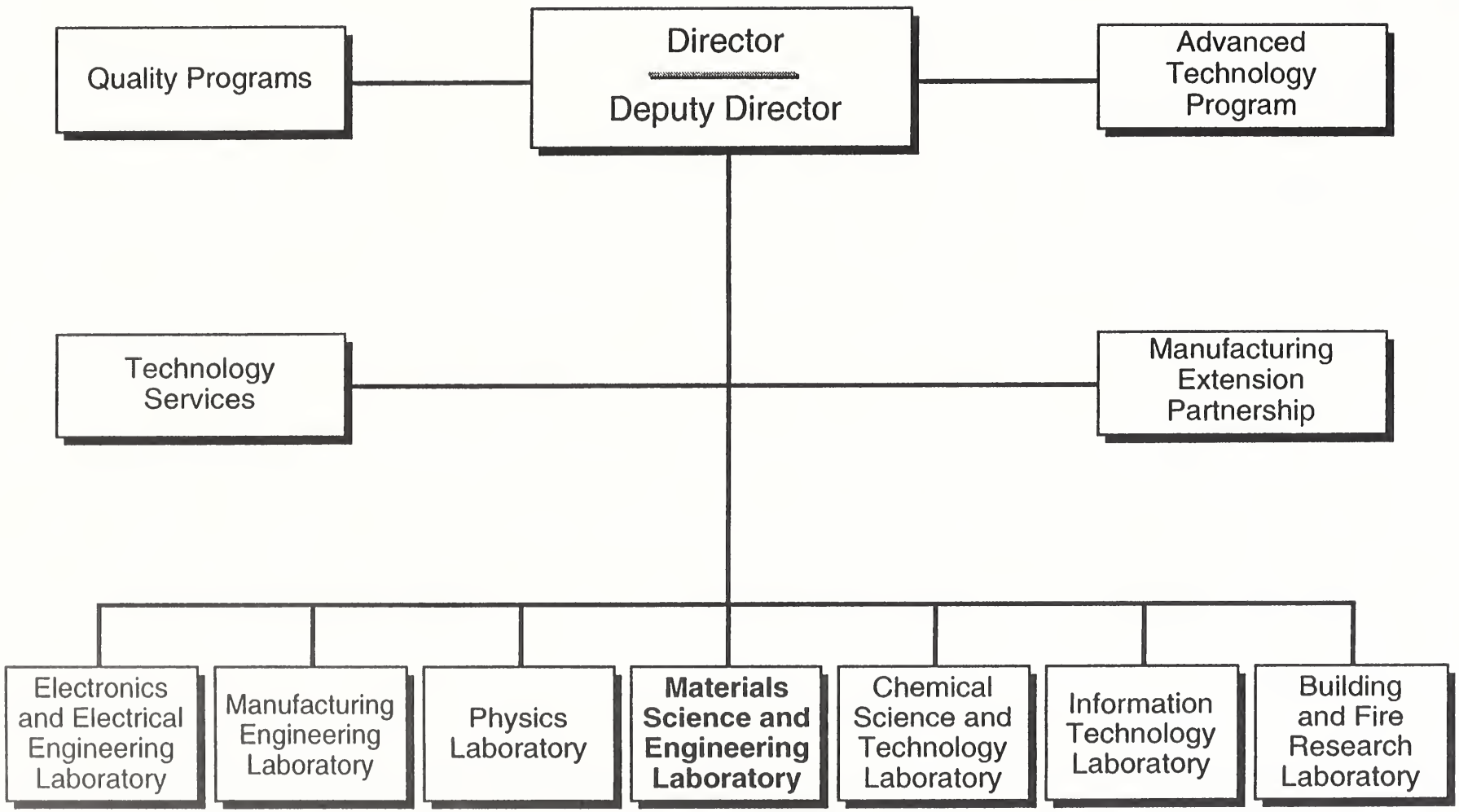
McMurdie, Howard	Joint Center for Powder Diffraction Studies
Nagarajan, Venkatta	Indian Institute of Science
Ondik, Helen	Consultant
Piermarini, Gasper	University of Maryland
Quinn, Janet	Consultant
Ritter, Joseph	Consultant
Roberts, Ellis	Consultant
Roth, Robert	Viper Group
Ruff, Arthur	Consultant
Saigel, Anil	Consultant
Shen, Ming	University of Illinois
Swab, Jeffrey	Army Research Laboratory
Swanson, Nils	American Ceramic Society
Turchinskaya, Marina	Consultant
Wachtman, John	Consultant
Wang, Tong	Jiao Tong University
Wang, Yinglong	University of Maryland
Wang, You	University of Illinois

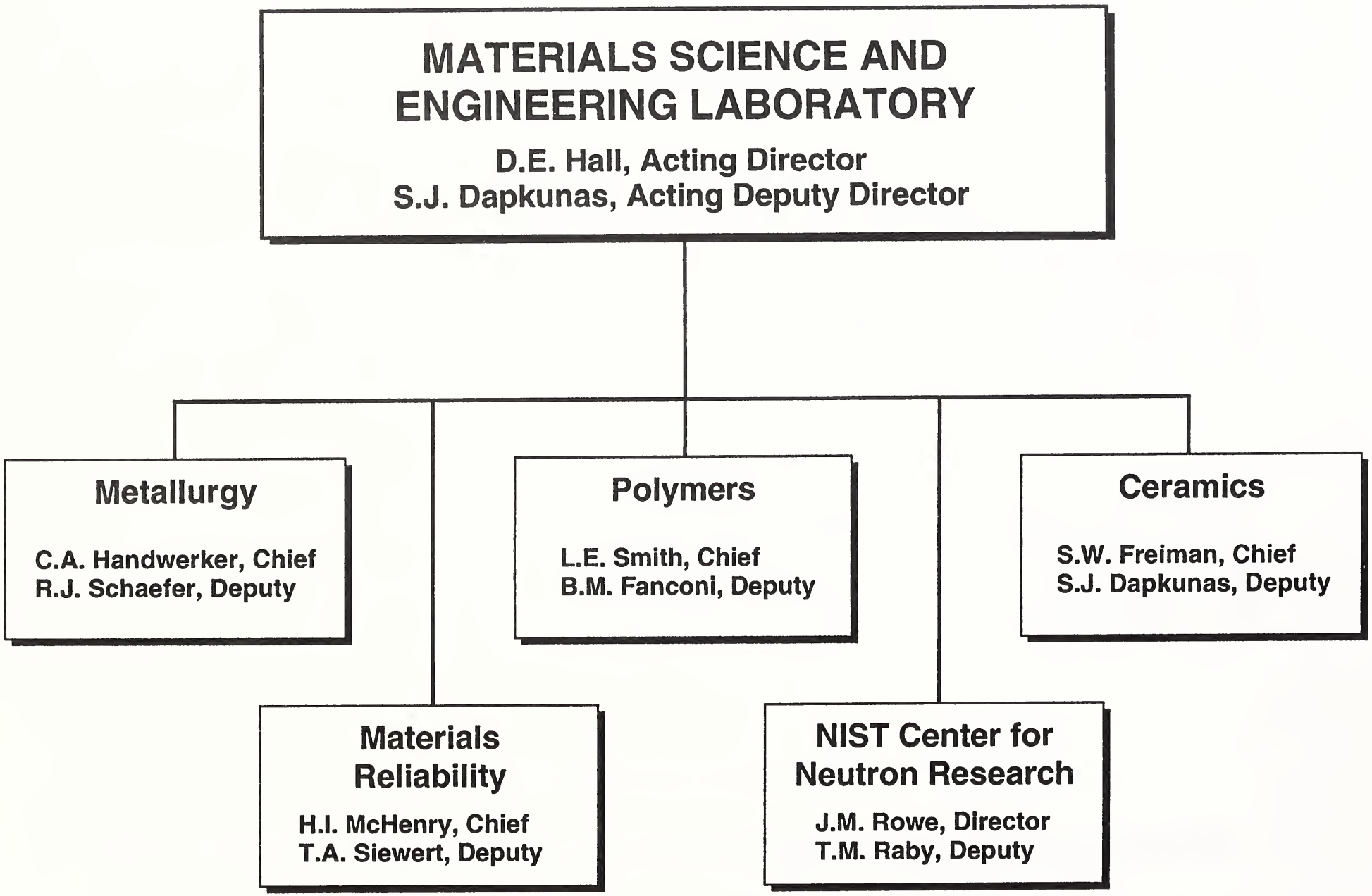
Wang, Zuoyi	University of Nebraska
Xu, Kang	Crystal Growth and Mat. Testing Assoc.
Ying, Tsi-Neng	University of Maryland
Ying, Zhanfeng	University of Illinois
Zhang, Jun	Lanzhou Institute of Chemical Physics
Zhang, Xian-Hua	University of Maryland

APPENDIX

National Institute of Standards and Technology

Organizational Chart

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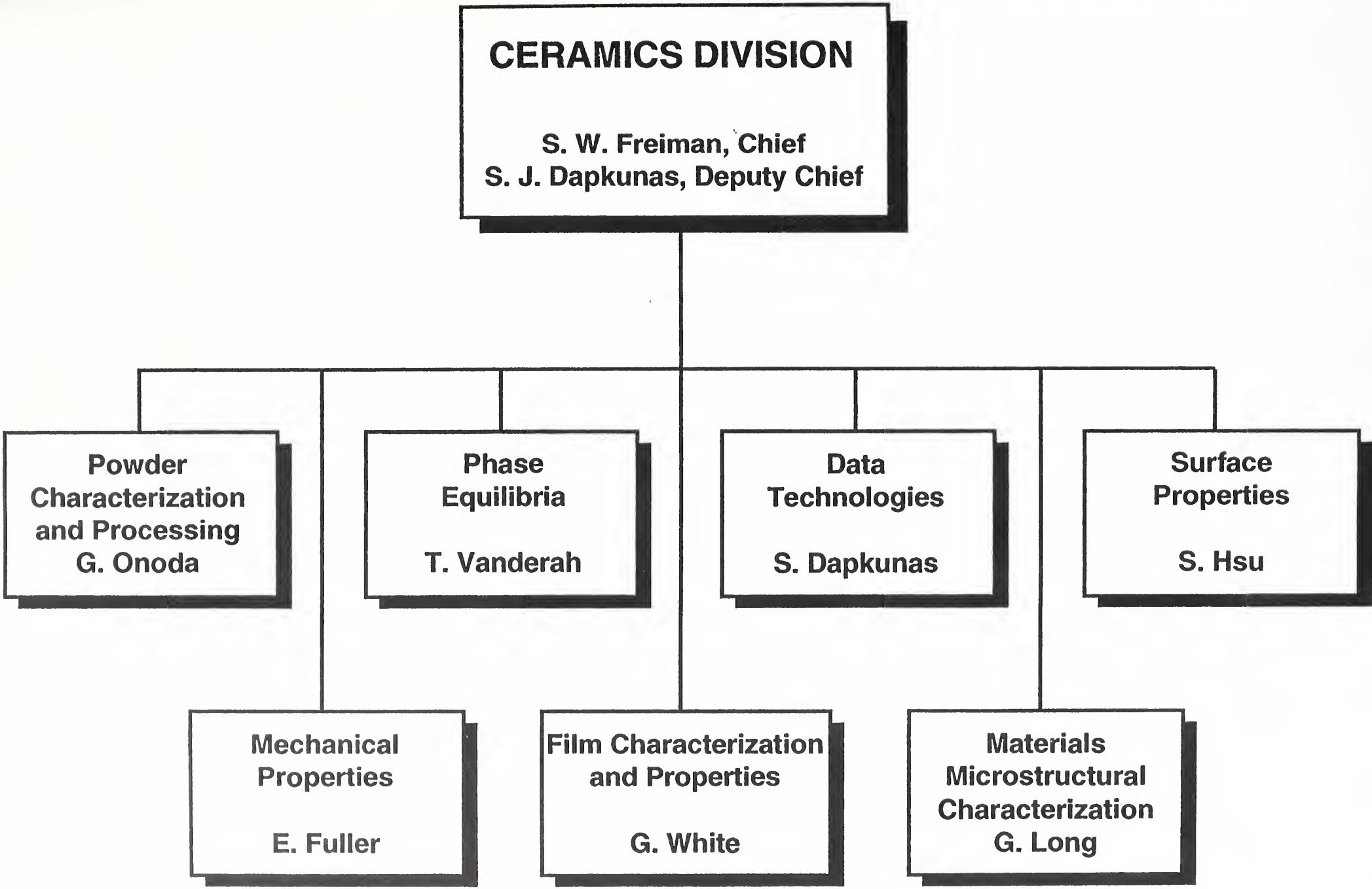
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